

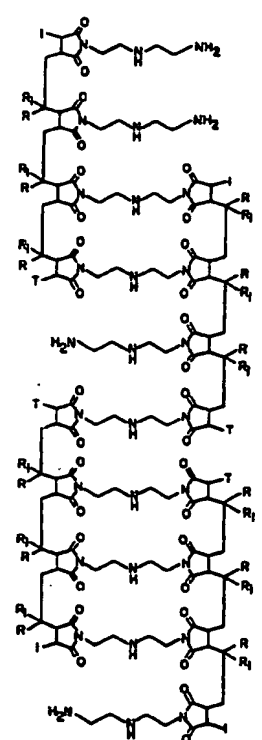
09

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification<sup>4</sup> : C07C 55/00, 69/34 C07D 307/34, C10M 129/93 C10L 1/18, 1/22</p>	<p>A1</p>	<p>(11) International Publication Number: <b>WO 90/03359</b>  (43) International Publication Date: 5 April 1990 (05.04.90)</p>
<p>(21) International Application Number: PCT/US89/04270 (22) International Filing Date: 29 September 1989 (29.09.89)  (30) Priority data: 251,613 29 September 1988 (29.09.88) US  (71) Applicant: CHEVRON RESEARCH COMPANY [US/ US]; P.O. Box 7141, San Francisco, CA 94120-7141 (US).  (72) Inventor: HARRISON, James, J. ; 12 Stonehaven Court, Novato, CA 94947 (US).  (74) Agents: CAROLI, Claude, J. et al.; Chevron Corporation, Law Department, P.O. Box 7141, San Francisco, CA 94120-7141 (US).</p>		<p>(81) Designated States: AT (European patent), AU, BE (Euro- pean patent), BR, CH (European patent), DE (European patent), DK, FI, FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent).  Published With international search report.</p>
<p>(54) Title: NOVEL POLYMERIC DISPERSANTS HAVING ALTERNATING POLYALKYLENE AND SUCCINIC GROUPS</p> <p>(57) Abstract</p> <p>Novel copolymers of unsaturated acidic reactants and high molecular weight olef- ins wherein at least 20 percent of the total high molecular weight olefin comprises the al- kylvinylidene isomer are useful as dispersants in lubricating oils and fuels and also may be used to prepare polysuccinimides and other post-treated additives useful in lubricating oils and fuels.</p> 		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MR	Mauritania
BE	Belgium	GA	Gabon	MW	Malawi
BF	Burkina Faso	GB	United Kingdom	NL	Netherlands
BG	Bulgaria	HU	Hungary	NO	Norway
BJ	Benin	IT	Italy	RO	Romania
BR	Brazil	JP	Japan	SD	Sudan
CA	Canada	KP	Democratic People's Republic of Korea	SE	Sweden
CF	Central African Republic	KR	Republic of Korea	SN	Senegal
CG	Congo	LI	Liechtenstein	SU	Soviet Union
CH	Switzerland	LK	Sri Lanka	TD	Chad
CM	Cameroon	LU	Luxembourg	TG	Togo
DE	Germany, Federal Republic of	MC	Monaco	US	United States of America
DK	Denmark				

01           NOVEL POLYMERIC DISPERSANTS HAVING ALTERNATING  
02           POLYALKYLENE AND SUCCINIC GROUPS

03  
04           BACKGROUND OF THE INVENTION

05  
06   The present invention relates to compositions which are  
07   useful as intermediates for dispersants used in lubricating  
08   oil compositions or as dispersants themselves. In addition,  
09   some of these compositions are useful in the preparation of  
10   novel high molecular weight dispersants which have superior  
11   dispersant properties for dispersing sludge and varnish and  
12   superior Viton Seal compatibility.

13  
14   The high molecular weight dispersants of the present  
15   invention also advantageously impart fluidity modifying  
16   properties to lubricating oil compositions which are suffi-  
17   cient to allow elimination of some proportion of viscosity  
18   index improver from multigrade lubricating oil compositions  
19   which contain these dispersants.

20  
21   Alkenyl-substituted succinic anhydrides have been used as  
22   dispersants. Such alkenyl-substituted succinic anhydrides  
23   have been prepared by two different processes, a thermal  
24   process (see, e.g., U.S. Patent No. 3,361,673) and a  
25   chlorination process (see, e.g., U.S. Patent No. 3,172,892).  
26   The polyisobutenyl succinic anhydride ("PIBSA") produced by  
27   the thermal process has been characterized as a monomer  
28   containing a double bond in the product. Although the exact  
29   structure of chlorination PIBSA has not been definitively  
30   determined, the chlorination process PIBAs have been charac-  
31   terized as monomers containing either a double bond, a ring,  
32   other than a succinic anhydride ring and/or chlorine in the  
33   product. [See J. Weill and B. Sillion, "Reaction of  
34   Chlorinated Polyisobutene with Maleic Anhydride: Mechanism

2

01 Catalysis by Dichloromaleic Anhydride", Revue de l'Institut  
02 Français du Pétrole, Vol. 40, No. 1, pp. 77-89  
03 (January-February, 1985).] Such compositions include  
04 one-to-one monomeric adducts (see, e.g., U.S. Patents  
05 Nos. 3,219,666; 3,381,022) as well as adducts having poly-  
06 alkenyl-derived substituents adducted with at least 1.3  
07 succinic groups per polyalkenyl-derived substituent (see,  
08 e.g., U.S. Patent No. 4,234,435).

09  
10 In addition, copolymers of maleic anhydrides and some ali-  
11 phatic alpha-olefins have been prepared. The polymers so  
12 produced were useful for a variety of purposes including  
13 dispersants for pigments and intermediates in the prepara-  
14 tion of polyesters by their reaction with polyols or poly-  
15 epoxides. However, olefins having more than about 30 carbon  
16 atoms were found to be relatively unreactive. (See, e.g.,  
17 U.S. Patents Nos. 3,461,108; 3,560,455; 3,560,456;  
18 3,560,457; 3,580,893; 3,706,704; 3,729,450; and 3,729,451).

19

20 SUMMARY OF THE INVENTION

21

22 The present invention is directed to novel compositions  
23 useful as additives which comprise copolymers of an unsatu-  
24 rated acidic reactant and high molecular weight olefin  
25 wherein at least about 20 percent of the total high  
26 molecular weight olefin comprises the alkylvinylidene  
27 isomer, said copolymers having alternating succinic and  
28 polyalkyl groups. The high molecular weight olefin has a  
29 sufficient number of carbon atoms such that the resulting  
30 copolymer is soluble in lubricating oil. Suitable olefins  
31 include those having about 32 carbon atoms or more (prefer-  
32 ably having about 52 carbon atoms or more). Those preferred  
33 high molecular weight olefins include polyisobutenes.  
34 Especially preferred are polyisobutenes having average

3

01 molecular weights of from about 500 to about 5000 and in  
02 which the alkylvinylidene isomer comprises at least 50  
03 percent of the total olefin.

04

05 These copolymers are useful as dispersants themselves and  
06 also as intermediates in the preparation of other dispersant  
07 additives having improved dispersancy and/or detergency  
08 properties when employed in a lubricating oil.

09

10 These copolymers are also advantageous because they do not  
11 contain double bonds, rings, other than succinic anhydride  
12 rings, or chlorine (in contrast to thermal and chlorination  
13 PIBSAs) and as such have improved stability, as well as  
14 improved environmental properties due to the absence of  
15 chlorine.

16

17 The present invention is also directed to polysuccinimides  
18 which are prepared by reacting a copolymer of the present  
19 invention with a polyamine to give a polysuccinimide. The  
20 present invention is directed to mono-polysuccinimides  
21 (where a polyamine component reacts with one succinic  
22 group); bis-polysuccinimides (where a polyamine component  
23 reacts with a succinic group from each of two copolymer  
24 molecules, thus effectively cross-linking the copolymer  
25 molecules); and higher polysuccinimides (where a polyamine  
26 component reacts with a succinic group from each of greater  
27 than 2 copolymer molecules). These polysuccinimides are  
28 useful as dispersants and/or detergents in fuels and oils.  
29 In addition, these polysuccinimides have advantageous vis-  
30 cosity modifying properties, and may provide a viscosity  
31 index credit ("V.I. Credit") when used in lubricating oils,  
32 which may permit elimination of some portion of viscosity  
33 index improver ("V.I. Improver") from multigrade lubricating  
34 oils containing the same.

---

4

01 In addition, the polysuccinimides of the present invention  
02 can form a ladder polymeric structure or a cross-linked  
03 polymeric structure. These structures are advantageous  
04 because it is believed such structures are more stable and  
05 resistant to hydrolytic degradation and also to degradation  
06 by shear stress.

07

08 In addition, the present invention is directed to modified  
09 polysuccinimides wherein one or more of the nitrogens of the  
10 polyamine component is substituted with a hydrocarbyl oxy-  
11 carbonyl, a hydroxyhydrocarbyl oxycarbonyl or a hydroxy  
12 poly(oxyalkylene)-oxycarbonyl. These modified polysuccini-  
13 mides are improved dispersants and/or detergents for use in  
14 fuels or oils.

15

16 Accordingly, the present invention also relates to a lubri-  
17 cating oil composition comprising a major amount of an oil  
18 of lubricating viscosity and an amount of a copolymer,  
19 polysuccinimide or modified succinimide additive of the  
20 present invention sufficient to provide dispersancy and/or  
21 detergency. The additives of the present invention may also  
22 be formulated in lubricating oil concentrates which comprise  
23 from about 90 to about 50 weight percent of an oil of lubri-  
24 cating viscosity and from about 10 to about 50 weight  
25 percent of an additive of the present invention.

26

27 Another composition aspect of the present invention is a  
28 fuel composition comprising a major portion of a fuel  
29 boiling in a gasoline or diesel range and an amount of  
30 copolymer, polysuccinimide or modified succinimide additives  
31 sufficient to provide dispersancy and/or detergency. The  
32 present invention is also directed to fuel concentrates  
33 comprising an inert stable oleophilic organic solvent  
34 boiling in the range of about 150°F to about 400°F and from

5

01 about 5 to about 50 weight percent of an additive of the  
02 present invention.

03

04 Definitions

05

06 As used herein, the following terms have the following  
07 meanings unless expressly stated to the contrary.

08

09 The term "unsaturated acidic reactants" refers to maleic or  
10 fumaric reactants of the general formula:

11

12

13



14

15 wherein X and X' are the same or different, provided that at  
16 least one of X and X' is a group that is capable of reacting  
17 to esterify alcohols, form amides or amine salts with ammo-  
18 nia or amines, form metal salts with reactive metals or  
19 basically reacting metal compounds and otherwise function as  
20 acylating agents. Typically, X and/or X' is -OH, -O-hydro-  
21 carbyl, -OM<sup>+</sup> where M<sup>+</sup> represents one equivalent of a metal,  
22 ammonium or amine cation, -NH<sub>2</sub>, -Cl, -Br, and taken together  
23 X and X' can be -O- so as to form an anhydride. Preferably  
24 X and X' are such that both carboxylic functions can enter  
25 into acylation reactions. Maleic anhydride is a preferred  
26 unsaturated acidic reactant. Other suitable unsaturated  
27 acidic reactants include electron-deficient olefins such as  
28 monophenyl maleic anhydride; monomethyl, dimethyl, mono-  
29 chloro, monobromo, monofluoro, dichloro and difluoro maleic  
30 anhydride; N-phenyl maleimide and other substituted  
31 maleimides; isomaleimides; fumaric acid, maleic acid, alkyl  
32 hydrogen maleates and fumarates, dialkyl fumarates and  
33 maleates, fumaronilic acids and maleanic acids; and  
34 maleonitrile, and fumaronitrile.

6

01 The term "alkylvinylidene" or "alkylvinylidene isomer"  
02 refers to high molecular weight olefins and polyalkylene  
03 components having the following vinylidene structure



08 wherein R is alkyl or substituted alkyl of sufficient chain  
09 length to give the resulting molecule solubility in lubri-  
10 cating oils and fuels, thus R generally has at least about  
11 30 carbon atoms, preferably at least about 50 carbon atoms  
12 and R<sub>V</sub> is lower alkyl of about 1 to about 6 carbon atoms.  
13

14 The term "soluble in lubricating oil" refers to the ability  
15 of a material to dissolve in aliphatic and aromatic hydro-  
16 carbons such as lubricating oils or fuels in essentially all  
17 proportions.  
18

19 The term "high molecular weight olefins" refers to olefins  
20 (including polymerized olefins having a residual unsatura-  
21 tion) of sufficient molecular weight and chain length to  
22 lend solubility in lubricating oil to their reaction prod-  
23 ucts. Typically olefins having about 32 carbons or greater  
24 (preferably olefins having about 52 carbons or more)  
25 suffice.  
26

27 The term "high molecular weight polyalkyl" refers to poly-  
28 alkyl groups of sufficient molecular weight and hydrocarbyl  
29 chain length that the products prepared having such groups  
30 are soluble in lubricating oil. Typically these high  
31 molecular weight polyalkyl groups have at least about 30  
32 carbon atoms, preferably at least about 50 carbon atoms.  
33 These high molecular weight polyalkyl groups may be derived  
34 from high molecular weight olefins.



7

01 The term "PIBSA" is an abbreviation for polyisobutenyl  
02 succinic anhydride.

03

04 The term "polyPIBSA" refers to a class of copolymers within  
05 the scope of the present invention which are copolymers of  
06 polyisobutene and an unsaturated acidic reactant which have  
07 alternating succinic groups and polyisobutyl groups.

08 PolyPIBSA has the general formula

09

10

11

12

13

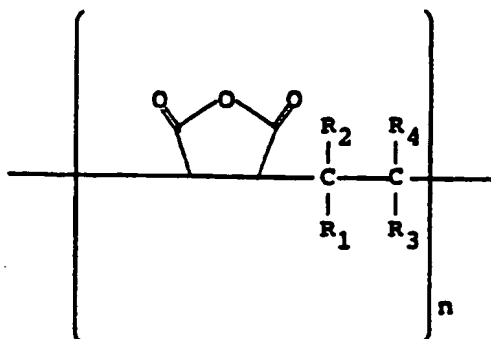
14

15

16

17

18



19 wherein  $n$  is one or greater;  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are selected from  
20 hydrogen, methyl and polyisobutyl having at least about 30 carbon  
21 atoms (preferably at least about 50 carbon atoms) wherein either  
22  $R_1$  and  $R_2$  are hydrogen and one of  $R_3$  and  $R_4$  is methyl and the  
23 other is polyisobutyl, or  $R_3$  and  $R_4$  are hydrogen and one of  $R_1$   
24 and  $R_2$  is methyl and the other is polyisobutyl.

25

26 The term "PIBSA number" refers to the anhydride (succinic group)  
27 content of polyPIBSA on a 100% actives basis. The PIBSA number  
28 is calculated by dividing the saponification number by the  
29 percent polyPIBSA in the product. The units are mg KOH per gram  
30 sample.

31

32

33

34

8

01 The term "succinic group" refers to a group having the formula

02

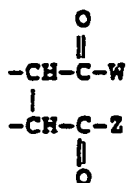
03

04

05

06

07



(IV)

08 wherein W and Z are independently selected from the group  
09 consisting of -OH, -Cl, -O- lower alkyl or taken together  
10 are -O- to form a succinic anhydride group.

11

12 The term "degree of polymerization" expresses the length of  
13 a linear polymer and refers to the number of repeating  
14 (monomeric) units in the chain. The average molecular  
15 weight of a polymer is the product of the degree of polymer-  
16 ization and the average molecular weight of the repeating  
17 unit (monomer). Accordingly, the average degree of poly-  
18 merization is calculated by dividing the average molecular  
19 weight of the polymer by the average molecular weight of the  
20 repeating unit.

21

22 The term "polysuccinimide" refers to the reaction product of  
23 a copolymer of the present invention with polyamine.

24

25

#### BRIEF DESCRIPTION OF THE DRAWING

26

27 FIG. 1 depicts one embodiment of a polysuccinimide of the  
28 present invention, wherein R is polyisobutyl, R<sub>1</sub> is lower  
29 alkyl, I is an initiator group and T is a terminator group.

30

31

32

33

34

01                    DETAILED DESCRIPTION OF THE INVENTION

02

03

A. COPOLYMER

04

05    The copolymers of the present invention are prepared by  
06    reacting a high molecular weight olefin wherein at least  
07    about 20% of the total olefin composition comprises the  
08    alkylvinylidene isomer and an unsaturated acidic reactant in  
09    the presence of a free radical initiator. Suitable high  
10    molecular weight olefins have a sufficient number of carbon  
11    atoms so that the resulting copolymer is soluble in  
12    lubricating oil and thus have on the order of about 32  
13    carbon atoms or more. Preferred high molecular weight of  
14    olefins are polyisobutenes and polypropylenes. Especially  
15    preferred are polyisobutenes, particularly preferred are  
16    those having a molecular weight of about 500 to about 5000,  
17    more preferably about 900 to about 2500. Preferred  
18    unsaturated acidic reactants include maleic anhydride.

19

20    Since the high molecular weight olefins used to prepare the  
21    copolymers of the present invention are generally mixtures  
22    of individual molecules of different molecular weights,  
23    individual copolymer molecules resulting will generally  
24    contain a mixture of high molecular weight polyalkyl groups  
25    of varying molecular weight. Also, mixtures of copolymer  
26    molecules having different degrees of polymerization will be  
27    produced.

28

29    The copolymers of the present invention have an average  
30    degree of polymerization of 1 or greater, preferably from  
31    about 1.1 to about 20, and more preferably from about 1.5 to  
32    about 10.

33

34

---

10

01 Among other factors, the present invention is based on my  
02 surprising finding that the reaction of these high molecular  
03 weight olefins wherein at least about 20% of the total  
04 composition comprises the methylvinylidene isomer with an  
05 unsaturated acidic reactant in the presence of a free  
06 radical initiator results in a copolymer having alternating  
07 polyalkylene and succinic groups. This is surprising in  
08 view of the teachings that reaction of polyalkenes, such as  
09 polyisobutenes, with unsaturated acidic reactants such as  
10 maleic anhydride, in the presence of a free radical  
11 initiator, resulted in a product similar to that produced by  
12 the thermal process for PIBSA which is a monomeric  
13 one-to-one adduct (see, e.g., U.S. Patent No. 3,367,864).  
14 It was taught that high molecular weight olefins were rela-  
15 tive unreactive under those conditions which was confirmed  
16 by my findings that reaction of polyisobutene prepared using  
17  $\text{AlCl}_3$  catalysis [in which the alkylvinylidene isomer com-  
18 prised a very small proportion (less than about 10%) of the  
19 total composition] with maleic anhydride in the presence of  
20 a free radical initiator resulted in low yield of product.  
21 In addition, the product obtained was similar to thermal  
22 PIBSA in molecular weight.

23

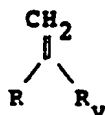
24 Thus, the copolymers of the present invention are prepared  
25 by reacting a "reactive" high molecular weight olefin in  
26 which a high proportion of unsaturation, at least about 20%  
27 is in the alkylvinylidene configuration, e.g.

28

29

30

31



32

33

34

wherein R and  $\text{R}_v$  are as previously defined in conjunction  
with Formula III, with an unsaturated acidic reactant in the  
presence of a free radical initiator. The product copolymer

11

01 has alternating polyalkylene and succinic groups and has an  
02 average degree of polymerization of 1 or greater.

03

04 The copolymers of the present invention have the general  
05 formula:

06

07

08

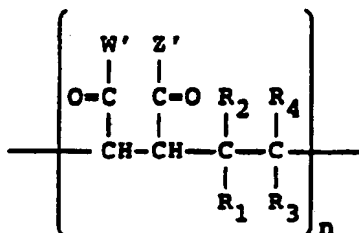
09

10

11

12

13



14 wherein W' and Z' are independently selected from the group  
15 consisting of -OH, -O- lower alkyl or taken together are -O-  
16 to form a succinic anhydride group, n is one or greater; and  
17 R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are selected from hydrogen, lower alkyl of  
18 1 to 6 carbon atoms, and high molecular weight polyalkyl  
19 wherein either R<sub>1</sub> and R<sub>2</sub> are hydrogen and one of R<sub>3</sub> and R<sub>4</sub>  
20 is lower alkyl and the other is high molecular weight poly-  
21 alkyl, or R<sub>3</sub> and R<sub>4</sub> are hydrogen and one of R<sub>1</sub> and R<sub>2</sub> is  
22 lower alkyl and the other is high molecular weight  
23 polyalkyl.

24

25 In a preferred embodiment, when maleic anhydride is used as  
26 the unsaturated acidic reactant, the reaction produces  
27 copolymers predominately of the following formula:

28

29

30

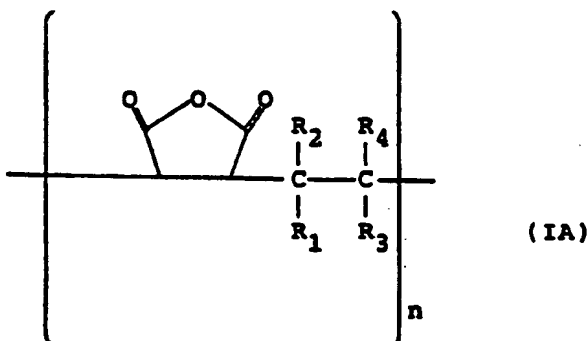
31

32

33

34

12



01  
02  
03  
04  
05  
06  
07  
08  
09  
10  
11

12 wherein n is about 1 to about 100, preferably about 2 to  
13 about 20, more preferably 2 to 10, and  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are  
14 selected from hydrogen, lower alkyl of about 1 to 6 carbon  
15 atoms and higher molecular weight polyalkyl, wherein either  
16  $R_1$  and  $R_2$  are hydrogen and one of  $R_3$  and  $R_4$  is lower alkyl  
17 and the other is high molecular weight polyalkyl or  $R_3$  and  
18  $R_4$  are hydrogen and one of  $R_1$  and  $R_2$  is lower alkyl and the  
19 other is high molecular weight polyalkyl.

20

21 Preferably, the high molecular weight polyalkyl group has at  
22 least about 30 carbon atoms (preferably at least about 50  
23 carbon atoms). Preferred high molecular weight polyalkyl  
24 groups include polyisobutyl groups. Preferred polyisobutyl  
25 groups include those having average molecular weights of  
26 about 500 to about 5000, more preferably from about 900 to  
27 about 2500. Preferred lower alkyl groups include methyl and  
28 ethyl; especially preferred lower alkyl groups include  
29 methyl.

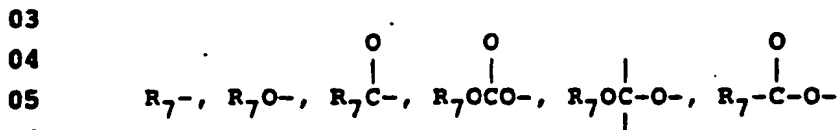
30

31 Generally, such copolymers contain an initiator group, I,  
32 and a terminator group, T, as a result of the reaction with  
33 the free radical initiator used in the polymerization

34

13

01 reaction. In such a case, the initiator and terminator  
 02 groups may be



07

08 where  $R_7$  is hydrogen, alkyl, aryl, alkaryl, cycloalkyl,  
 09 alkoxy, cycloalkoxy, acyl, alkenyl, cycloalkenyl, alkynyl;  
 10 or alkyl, aryl or alkaryl optionally substituted with 1 to  
 11 4 substituents independently selected from nitrile, keto,  
 12 halogen, nitro, alkyl, aryl, and the like. Alternatively,  
 13 the initiator group and/or terminator group may be derived  
 14 from the reaction product of the initiator with another  
 15 material such as solvent; for example, the initiator may  
 16 react with toluene to produce a benzyl radical.

17

18 The copolymers of the present invention differ from the  
 19 PIBSAs prepared by the thermal process in that the thermal  
 20 process products contain a double bond and a singly substi-  
 21 tuted succinic anhydride group. The copolymers of the  
 22 present invention differ from the PIBSAs prepared by the  
 23 chlorination process, since those products contain a double  
 24 bond, a ring, other than a succinic anhydride ring or one or  
 25 more chlorine atoms.

26

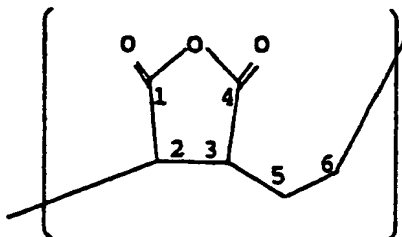
27 The copolymers of the present invention contain no double  
 28 bonds, rings, other than succinic anhydride rings, or  
 29 chlorine atoms. In addition, the succinic anhydride groups  
 30 are doubly substituted (i.e., have two substituents, one of  
 31 which may be hydrogen) at the 2- and 3-positions, that is:

32

33

34

14



A(1) High Molecular Weight Polyalkylene Group

The high molecular weight polyalkyl group is derived from a high molecular weight olefin. The high molecular weight olefins used in the preparation of the copolymers of the present invention are of sufficiently long chain length so that the resulting composition is soluble in and compatible with mineral oils, fuels and the like; and the alkylvinylidene isomer of the high molecular weight olefin comprises at least about 20% of the total olefin composition.

Such high molecular weight olefins are generally mixtures of molecules having different molecular weights and can have at least one branch per 6 carbon atoms along the chain, preferably at least one branch per 4 carbon atoms along the chain, and particularly preferred that there be about one branch per 2 carbon atoms along the chain. These branched chain olefins may conveniently comprise polyalkenes prepared by the polymerization of olefins of from 3 to 6 carbon atoms, and preferably from olefins of from 3 to 4 carbon atoms, and more preferably from propylene or isobutylene. The addition-polymerizable olefins employed are normally 1-olefins. The branch may be of from 1 to 4 carbon atoms, more usually of from 1 to 2 carbon atoms and preferably methyl.



15

01 The preferred alkylvinylidene isomer comprises a methyl- or  
02 ethylvinylidene isomer, more preferably the methylvinylidene  
03 isomer.

04

05 The especially preferred high molecular weight olefins used  
06 to prepare the copolymers of the present invention are poly-  
07 isobutenes which comprise at least about 20% of the more  
08 reactive methylvinylidene isomer, preferably at least 50%  
09 and more preferably at least 70%. Suitable polyisobutenes  
10 include those prepared using  $\text{BF}_3$  catalysis. The preparation  
11 of such polyisobutenes in which the methylvinylidene isomer  
12 comprises a high percentage of the total composition is  
13 described in U.S. Patents Nos. 4,152,499 and 4,605,808.

14

15 Polyisobutenes produced by conventional  $\text{AlCl}_3$  catalysis when  
16 reacted with unsaturated acidic reactants, such as maleic  
17 anhydride, in the presence of a free radical initiator,  
18 produce products similar to thermal PIBSA in molecular  
19 weight and thus do not produce a copolymeric product.

20

21 Preferred are polyisobutenes having average molecular  
22 weights of about 500 to about 5000. Especially preferred  
23 are those having average molecular weights of about 900 to  
24 about 2500.

25

## 26 A(2) Unsaturated Acidic Reactant

27

28 The unsaturated acidic reactant used in the preparation of  
29 the copolymers of the present invention comprises a maleic  
30 or fumaric reactant of the general formula:

31

32

33

34



16

01 wherein X and X' are the same or different, provided that at  
02 least one of X and X' is a group that is capable of reacting  
03 to esterify alcohols, form amides or amine salts with ammo-  
04 nia or amines, form metal salts with reactive metals or  
05 basically reacting metal compounds and otherwise function to  
06 acylate. Typically, X and/or X' is -OH, -O-hydrocarbyl,  
07 -OM<sup>+</sup> where M<sup>+</sup> represents one equivalent of a metal, ammonium  
08 or amine cation, -NH<sub>2</sub>, -Cl, -Br, and taken together X and X'  
09 can be -O- so as to form an anhydride. Preferably, X and X'  
10 are such that both carboxylic functions can enter into  
11 acylation reactions. Preferred are acidic reactants where X  
12 and X' are each independently selected from the group con-  
13 sisting of -OH, -Cl, -O- lower alkyl and when taken  
14 together, X and X' are -O-. Maleic anhydride is the pre-  
15 ferred acidic reactant. Other suitable acidic reactants  
16 include electron-deficient olefins such as monophenyl maleic  
17 anhydride; monomethyl, dimethyl, monochloro, monobromo,  
18 monofluoro, dichloro and difluoro maleic anhydride; N-phenyl  
19 maleimide and other substituted maleimides; isomaleimides;  
20 fumaric acid, maleic acid, alkyl hydrogen maleates and  
21 fumarates, dialkyl fumarates and maleates, fumaronilic acids  
22 and maleonic acids; and maleonitrile, and fumaronitrile.  
23  
24 Preferred unsaturated acidic reactants include maleic  
25 anhydride, and maleic acid. The particularly preferred  
26 acidic reactant is maleic anhydride.

### 27 A(3) General Preparation of Copolymer

28  
29  
30 As noted above, the copolymers of the present invention are  
31 prepared by reacting a reactive high molecular weight olefin  
32 and an unsaturated acidic reactant in the presence of a free  
33 radical initiator.  
34

01 The reaction may be conducted at a temperature of about  
02 -30°C to about 210°C, preferably from about 40°C to about  
03 150°C. I have found that degree of polymerization is  
04 inversely proportional to temperature. Accordingly, for the  
05 preferred high molecular weight copolymers, it is advan-  
06 tageous to employ lower reaction temperatures. For example,  
07 if the reaction is conducted at about 138°C, an average  
08 degree of polymerization of about 1.3 was obtained. How-  
09 ever, if the reaction was conducted at a temperature of  
10 about 40°C, an average degree of polymerization of about  
11 10.5 was obtained.

12

13 The reaction may be conducted neat, that is, both the high  
14 molecular weight olefin, and acidic reactant and the free  
15 radical initiator are combined in the proper ratio, and then  
16 stirred at the reaction temperature.

17

18 Alternatively, the reaction may be conducted in a diluent.  
19 For example, the reactants may be combined in a solvent.  
20 Suitable solvents include those in which the reactants and  
21 free radical initiator are soluble and include acetone,  
22 tetrahydrofuran, chloroform, methylene chloride, dichloro-  
23 ethane, toluene, dioxane, chlorobenzene, xylenes, or the  
24 like. After the reaction is complete, volatile components  
25 may be stripped off. When a diluent is employed, it is  
26 preferably inert to the reactants and products formed and is  
27 generally used in an amount sufficient to ensure efficient  
28 stirring.

29

30 Moreover, my colleague W. R. Ruhe, has discovered that in  
31 the preparation of polyPIBSA, improved results are obtained  
32 by using PIBSA or polyPIBSA as a solvent for the reaction.  
33 (See, e.g., Examples 16, 17A and 17B herein.)

34

01 In general, the copolymerization can be initiated by any  
02 free radical initiator. Such initiators are well known in  
03 the art. However, the choice of free radical initiator may  
04 be influenced by the reaction temperature employed.

05  
06 The preferred free-radical initiators are the peroxide-type  
07 polymerization initiators and the azo-type polymerization  
08 initiators. Radiation can also be used to initiate the  
09 reaction, if desired.

10  
11 The peroxide-type free-radical initiator can be organic or  
12 inorganic, the organic having the general formula:  $R_3OOR_3'$   
13 where  $R_3$  is any organic radical and  $R_3'$  is selected from the  
14 group consisting of hydrogen and any organic radical. Both  
15  $R_3$  and  $R_3'$  can be organic radicals, preferably hydrocarbon,  
16 aroyl, and acyl radicals, carrying, if desired, substituents  
17 such as halogens, etc. Preferred peroxides include  
18 di-tert-butyl peroxide, tert-butyl peroxybenzoate, and  
19 dicumyl peroxide.

20  
21 Examples of other suitable peroxides, which in no way are  
22 limiting, include benzoyl peroxide; lauroyl peroxide; other  
23 tertiary butyl peroxides; 2,4-dichlorobenzoyl peroxide;  
24 tertiary butyl hydroperoxide; cumene hydroperoxide; diacetyl  
25 peroxide; acetyl hydroperoxide; diethylperoxycarbonate;  
26 tertiary butyl perbenzoate; and the like.

27  
28 The azo-type compounds, typified by alpha,alpha'-azo-  
29 bisisobutyronitrile, are also well-known free-radical  
30 promoting materials. These azo compounds can be defined as  
31 those having present in the molecule group  $-N=N$  wherein the  
32 balances are satisfied by organic radicals, at least one of  
33 which is preferably attached to a tertiary carbon. Other  
34 suitable azo compounds include, but are not limited to,

01 p-bromobenzenediazonium fluoborate; p-tolyldiazoaminoben-  
02 zene; p-bromobenzenediazonium hydroxide; azomethane and  
03 phenyldiazonium halides. A suitable list of azo-type com-  
04 pounds can be found in U.S. Patent No. 2,551,813, issued  
05 May 8, 1951 to Paul Pinkney.

06

07 The amount of initiator to employ, exclusive of radiation,  
08 of course, depends to a large extent on the particular  
09 initiator chose, the high molecular olefin used and the  
10 reaction conditions. The initiator must, of course, be  
11 soluble in the reaction medium. The usual concentrations of  
12 initiator are between 0.001:1 and 0.2:1 moles of initiator  
13 per mole of acidic reactant, with preferred amounts between  
14 0.005:1 and 0.10:1.

15

16 The polymerization temperature must be sufficiently high to  
17 break down the initiator to produce the desired free-radi-  
18 cals. For example, using benzoyl peroxide as the initiator,  
19 the reaction temperature can be between about 75°C and about  
20 90°C, preferably between about 80°C and about 85°C. Higher  
21 and lower temperatures can be employed, a suitable broad  
22 range of temperatures being between about 20°C and about  
23 200°C, with preferred temperatures between about 50°C and  
24 about 150°C.

25

26 The reaction pressure should be sufficient to maintain the  
27 solvent in the liquid phase. Pressures can therefore vary  
28 between about atmospheric and 100 psig or higher, but the  
29 preferred pressure is atmospheric.

30

31 The reaction time is usually sufficient to result in the  
32 substantially complete conversion of the acidic reactant and  
33 high molecular weight olefin to copolymer. The reaction

34

---

01 time is suitable between one and 24 hours, with preferred  
02 reaction times between two and ten hours.  
03  
04 As noted above, the subject reaction is a solution-type  
05 polymerization reaction. The high molecular weight olefin,  
06 acidic reactant, solvent and initiator can be brought  
07 together in any suitable manner. The important factors are  
08 intimate contact of the high molecular weight olefin and  
09 acidic reactant in the presence of a free-radical producing  
10 material. The reaction, for example, can be conducted in a  
11 batch system where the high molecular weight olefin is added  
12 all initially to a mixture of acidic reactant, initiator and  
13 solvent or the high molecular weight olefin can be added  
14 intermittently or continuously to the reaction pot. Alter-  
15 natively, the reactants may be combined in other orders; for  
16 example, acidic reactant and initiator may be added to high  
17 molecular weight olefin and solvent in the reaction pot. In  
18 another manner, the components in the reaction mixture can  
19 be added continuously to a stirred reactor with continuous  
20 removal of a portion of the product to a recovery train or  
21 to other reactors in series. The reaction can also suit-  
22 ably take place in a coil-type reactor where the components  
23 are added at one or more points along the coil.  
24  
25 In one envisioned embodiment, the reaction product of an  
26 unsaturated acidic reactant and a high molecular weight,  
27 high vinylidene-containing olefin is further reacted  
28 thermally. In this embodiment, any unreacted olefin,  
29 generally the more hindered olefins, i.e., the non-vinyl-  
30 idene, that do not react readily with the unsaturated acidic  
31 reactant under free radical conditions are reacted with  
32 unsaturated acidic reactant under thermal conditions, i.e.,  
33 at temperatures of about 180° to 280°C. These conditions  
34

21

01 are similar to those used for preparing thermal process  
02 PIBSA.

03

04 The reaction solvent, as noted above, must be one which  
05 dissolves both the acidic reactant and the high molecular  
06 weight olefin. It is necessary to dissolve the acidic  
07 reactant and high molecular weight olefin so as to bring  
08 them into intimate contact in the solution polymerization  
09 reaction. It has been found that the solvent must also be  
10 one in which the resultant copolymers are soluble.

11

12 Suitable solvents include liquid saturated or aromatic  
13 hydrocarbons having from six to 20 carbon atoms; ketones  
14 having from three to five carbon atoms; and liquid saturated  
15 aliphatic dihalogenated hydrocarbons having from one to five  
16 carbon atoms per molecule, preferably from one to three car-  
17 bon atoms per molecule. By "liquid" is meant liquid under  
18 the conditions of polymerization. In the dihalogenated  
19 hydrocarbons, the halogens are preferably on adjacent carbon  
20 atoms. By "halogen" is meant F, Cl and Br. The amount of  
21 solvent must be such that it can dissolve the acidic reac-  
22 tant and high molecular weight olefin in addition to the  
23 resulting copolymers. The volume ratio of solvent to high  
24 molecular weight olefin is suitably between 1:1 and 100:1  
25 and is preferably between 1.5:1 and 4:1.

26

27 Suitable solvents include the ketones having from three to  
28 six carbon atoms and the saturated dichlorinated hydro-  
29 carbons having from one to five, more preferably one to  
30 three, carbon atoms.

31

32 Examples of suitable solvents include, but are not limited  
33 to:

34

22

- 01 1. ketones, such as: acetone; methylethylketone;  
02 diethylketone; and methylisobutylketone;  
03  
04 2. aromatic hydrocarbons, such as: benzene; xylene; and  
05 toluene;  
06  
07 3. saturated dihalogenated hydrocarbons, such as:  
08 dichloromethane; dibromomethane; 1-bromo-2-chloroethane;  
09 1,1-dibromoethane; 1,1-dichloroethane;  
10 1,2-dichloroethane; 1,3-dibromopropane;  
11 1,2-dibromopropane; 1,2-dibromo-2-methylpropane;  
12 1,2-dichloropropane; 1,1-dichloropropane;  
13 1,3-dichloropropane; 1-bromo-2-chloropropane;  
14 1,2-dichlorobutane; 1,5-dibromopentane; and  
15 1,5-dichloropentane; or  
16  
17 4. mixtures of the above, such as: benzene-  
18 methylethylketone.  
19

20 As noted previously, W. R. Ruhe has discovered that use of a  
21 mixture of copolymer and polyisobutene as a solvent results  
22 in improved yields and advantageously dissolves the acidic  
23 reactant when used as a reaction medium.  
24

25 The copolymer is conveniently separated from solvent and  
26 unreacted acidic reactant by conventional procedures such as  
27 phase separation, solvent distillation, precipitation and  
28 the like. If desired, dispersing agents and/or cosolvents  
29 may be used during the reaction.  
30

31 The isolated copolymer may then be reacted with a polyamine  
32 to form a polymeric succinimide. The preparation and  
33  
34



23

01 characterization of such polysuccinimides and their treat-  
02 ment with other agents to give other dispersant compositions  
03 is described herein.

04

05

#### A(4) Preferred Copolymers

06

07 Preferred copolymers include those where an unsaturated  
08 acidic reactant, most preferably maleic anhydride, is  
09 copolymerized with a "reactive" polyisobutene, in which at  
10 least about 50 percent or more of the polyisobutene com-  
11 prises the alkylvinylidene, more preferably, the methyl-  
12 vinylidene, isomer, to give a "polyPIBSA".

13

14 Preferred are polyPIBSAs wherein the polyisobutyl group has  
15 an average molecular weight of about 500 to about 5000, more  
16 preferably from about 950 to about 2500. Preferred are  
17 polyPIBSAs having an average degree of polymerization of  
18 about 1.1 to about 20, more preferably from about 1.5 to  
19 about 10.

20

21

#### B. POLYSUCCINIMIDES

22

23 The polyamino polysuccinimides of the present invention are  
24 prepared by reacting a copolymer of the present invention  
25 with a polyamine. Polysuccinimides which may be prepared  
26 include monopolysuccinimides (where a polyamine component  
27 reacts with one succinic group), bis-polysuccinimides (where  
28 a polyamine component reacts with a succinic group from each  
29 of two copolymer molecules), higher succinimides (where a  
30 polyamine component reacts with a succinic group from each  
31 of more than 2 copolymer molecules) or mixtures thereof.  
32 The polysuccinimide(s) produced may depend on the charge  
33 mole ratio of polyamine to succinic groups in the copolymer  
34 molecule and the particular polyamine used. Using a charge

24

01 mole ratio of polyamine to succinic groups in copolymer of  
02 about 1.0, predominately monopolysuccinimide is obtained.  
03 Charge mole ratios of polyamine to succinic group in copoly-  
04 mer of about 1:2 may produce predominately bis-polysucci-  
05 nimide. Higher polysuccinimides may be produced if there is  
06 branching in the polyamine so that it may react with a  
07 succinic group from each of greater than 2 copolymer  
08 molecules.

09

10

#### B(1) Preferred Copolymers

11

12 Preferred copolymers include polyPIBSAs prepared according  
13 to the present invention as described hereinabove.

14

15 Preferred polyPIBSAs include those prepared using a poly-  
16 isobutene of average molecular weight of about 500 to about  
17 5000, preferably of about 950 to about 2500 and wherein at  
18 least about 50 percent of the total polyisobutene comprises  
19 the alkylvinylidene isomer. Preferred alkylvinylidene  
20 isomers include methylvinylidene and ethylvinylidene.  
21 Especially preferred is methylvinylidene. Preferred are  
22 polyPIBSAs having an average degree of polymerization of  
23 about 1.1 to about 15. Particularly preferred polyPIBSAs  
24 have an average degree of polymerization of about 1.5 to  
25 about 10, and which are prepared using a polyisobutene  
26 having an average molecular weight of about 900 to about  
27 2500.

28

29

#### B(2) Polyamine

30

31 The polyamine employed to prepare the polyamino poly-  
32 succinimides is preferably polyamine having from 2 to about  
33 12 amine nitrogen atoms and from 2 to about 40 carbon atoms.  
34 The polyamine is reacted with polyPIBSA to produce the poly-

25

01 amino polysuccinimide, employed in this invention. The  
02 polyamine is so selected so as to provide at least one basic  
03 amine per succinimide group. Since the reaction of a  
04 nitrogen of a polyamino polysuccinimide to form a hydro-  
05 carbyl oxycarbonyl, a hydroxy hydrocarbyl oxycarbonyl or a  
06 hydroxy polyoxyalkylene oxycarbonyl is believed to effi-  
07 ciently proceed through a secondary or primary amine, at  
08 least one of the basic amine atoms of the polyamino poly-  
09 succinimide must either be a primary amine or a secondary  
10 amine. Accordingly, in those instances in which the  
11 succinimide group contains only one basic amine, that amine  
12 must either be a primary amine or a secondary amine. The  
13 polyamine preferably has a carbon-to-nitrogen ratio of from  
14 about 1:1 to about 10:1.

15

16 The polyamine portion of the polyamino polysuccinimide may  
17 be substituted with substituents selected from (a) hydrogen,  
18 (b) hydrocarbyl groups of from 1 to about 10 carbon atoms,  
19 (c) acyl groups of from 2 to about 10 carbon atoms, and  
20 (d) monoketo, monohydroxy, mononitro, monocyano, lower alkyl  
21 and lower alkoxy derivatives of (b) and (c). "Lower", as  
22 used in terms like "lower alkyl" or "lower alkoxy", means a  
23 group containing from 1 to about 6 carbon atoms. At least  
24 one of the substituents on one of the amines of the  
25 polyamine is hydrogen, e.g., at least one of the basic  
26 nitrogen atoms of the polyamine is a primary or secondary  
27 amino nitrogen atom.

28

29 Hydrocarbyl, as used in describing the polyamine components  
30 of this invention, denotes an organic radical composed of  
31 carbon and hydrogen which may be aliphatic, alicyclic,  
32 aromatic or combinations thereof, e.g., aralkyl. Prefer-  
33 ably, the hydrocarbyl group will be relatively free of  
34 aliphatic unsaturation, i.e., ethylenic and acetylenic,

---

26

01 particularly acetylenic unsaturation. The substituted  
02 polyamines of the present invention are generally, but not  
03 necessarily, N-substituted polyamines. Exemplary hydro-  
04 carbyl groups and substituted hydrocarbyl groups include  
05 alkyls such as methyl, ethyl, propyl, butyl, isobutyl,  
06 pentyl, hexyl, octyl, etc., alkenyls such as propenyl,  
07 isobutenyl, hexenyl, octenyl, etc., hydroxyalkyls, such as  
08 2-hydroxyethyl, 3-hydroxypropyl, hydroxyisopropyl,  
09 4-hydroxybutyl, etc. ketoalkyls, such as 2-ketopropyl,  
10 6-ketooctyl, etc., alkoxy and lower alkenoxy alkyls, such as  
11 ethoxyethyl, ethoxypropyl, propoxyethyl, propoxypropyl,  
12 2-(2-ethoxyethoxy)ethyl, 2-(2-(2-ethoxy-ethoxy)ethoxy)ethyl,  
13 3,6,9,12-tetraoxatetradecyl, 2-(2-ethoxyethoxy)hexyl, etc.  
14 The acyl groups of the aforementioned (c) substituents are  
15 such as propionyl, acetyl, etc. The more preferred substitu-  
16 ents are hydrogen, C<sub>1</sub>-C<sub>6</sub> alkyls and C<sub>1</sub>-C<sub>6</sub> hydroxyalkyls.

17  
18 In a substituted polyamine the substituents are found at any  
19 atom capable of receiving them. The substituted atoms,  
20 e.g., substituted nitrogen atoms, are generally geometri-  
21 cally inequivalent, and consequently the substituted amines  
22 finding use in the present invention can be mixtures of  
23 mono- and polysubstituted polyamines with substituent groups  
24 situated at equivalent and/or inequivalent atoms.

25  
26 The more preferred polyamine finding use within the scope of  
27 the present invention is a polyalkylene polyamine, including  
28 alkylene diamine, and including substituted polyamines,  
29 e.g., alkyl substituted polyalkylene polyamine. Preferably,  
30 the alkylene group contains from 2 to 6 carbon atoms, there  
31 being preferably from 2 to 3 carbon atoms between the  
32 nitrogen atoms. Such groups are exemplified by ethylene,  
33 1,2-propylene, 2,2-dimethylpropylene, trimethylene, etc.  
34 Examples of such polyamines include ethylene diamine,

27

01 diethylene triamine, di(trimethylene)triamine, dipropylene  
02 triamine, triethylene tetramine, tripropylene tetramine,  
03 tetraethylene pentamine, and pentaethylene hexamine. Such  
04 amines encompass isomers such as branched-chain polyamine  
05 and the previously mentioned substituted polyamines,  
06 including hydrocarbyl-substituted polyamines. Among the  
07 polyalkylene polyamines, those containing 2-12 amine  
08 nitrogen atoms and 2-24 carbon atoms are especially  
09 preferred, and the C<sub>2</sub>-C<sub>5</sub> alkylene polyamines are most  
10 preferred, in particular, the lower polyalkylene polyamines,  
11 e.g., ethylene diamine, dipropylene triamine, etc.

12  
13 Preferred polyamines also include heavy polyamines such as  
14 polyamine HPA available from Union Carbide.

15  
16 The polyamine component also may contain heterocyclic poly-  
17 amines, heterocyclic substituted amines and substituted  
18 heterocyclic compounds, wherein the heterocycle comprises  
19 one or more 5 to 6-membered rings containing oxygen and/or  
20 nitrogen. Such heterocycles may be saturated or unsaturated  
21 and substituted with groups selected from the aforementioned  
22 (a), (b), (c) and (d). The heterocycles are exemplified by  
23 piperazines, such as 2-methylpiperazine, N-(2-hydroxyethyl)-  
24 piperazine, 1,2-bis-(n-piperazinyl)ethane, and N,N'-bis(N-  
25 piperazinyl)piperazine, 2-methylimidazoline, 3-amino-  
26 piperidine, 2-aminopyridine, 2-(3-aminoethyl)-3-pyrroline,  
27 3-aminopyrrolidine, N-(3-aminopropyl)-morpholine, etc.  
28 Among the heterocyclic compounds, the piperazines are  
29 preferred.

30  
31 Typical polyamines that can be used to form the compounds of  
32 this invention include the following:

33  
34

---

28

01 ethylene diamine, 1,2-propylene diamine, 1,3-propylene  
02 diamine, diethylene triamine, triethylene tetramine,  
03 hexamethylene diamine, tetraethylene pentamine, methyl-  
04 aminopropylene diamine, N-(betaaminoethyl)piperazine,  
05 N,N'-di(betaaminoethyl)piperazine, N,N'-di(beta-amino-  
06 ethyl)-imidazolidone-2, N-(beta-cyanoethyl)ethane-1,2-  
07 diamine, 1,3,6,9-tetraaminooctadecane, 1,3,6-triamino-9-  
08 oxadecane, N-(beta-aminoethyl)diethanolamine, N-methyl-1,2-  
09 propanediamine, 2-(2-aminoethylamino)-ethanol, 2-[2-(2-amino-  
10 ethylamino)ethylamino]-ethanol.

11

12 Another group of suitable polyamines are the propylene-  
13 amines, (bisaminopropylethylenediamines). Propyleneamines  
14 are prepared by the reaction of acrylonitrile with an  
15 ethyleneamine, for example, an ethyleneamine having the  
16 formula  $H_2N(CH_2CH_2NH)_jH$  wherein  $j$  is an integer from 1 to 5,  
17 followed by hydrogenation of the resultant intermediate.  
18 Thus, the product prepared from ethylene diamine and  
19 acrylonitrile would be  $H_2N(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$ .

20

21 In many instances the polyamine used as a reactant in the  
22 production of polysuccinimides of the present invention is  
23 not a single compound but a mixture in which one or several  
24 compounds predominate with the average composition indi-  
25 cated. For example, tetraethylene pentamine prepared by the  
26 polymerization of aziridine or the reaction of dichloro-  
27 ethylene and ammonia will have both lower and higher amine  
28 members, e.g., triethylene tetramine, substituted  
29 piperazines and pentaethylene hexamine, but the composition  
30 will be largely tetraethylene pentamine and the empirical  
31 formula of the total amine composition will closely  
32 approximate that of tetraethylene pentamine. Finally, in  
33 preparing the polysuccinimide for use in this invention,  
34 where the various nitrogen atoms of the polyamine are not

29

01 geometrically equivalent, several substitutional isomers are  
02 possible and are encompassed within the final product.  
03 Methods of preparation of polyamines and their reactions are  
04 detailed in Sidgewick's "The Organic Chemistry of Nitrogen",  
05 Clarendon Press, Oxford, 1966; Noller's "Chemistry of  
06 Organic Compounds", Saunders, Philadelphia, 2nd Ed., 1957;  
07 and Kirk-Othmer's "Encyclopedia of Chemical Technology", 2nd  
08 Ed., especially Volume 2, pp. 99-116.

09

10

### B(3) General Preparation

11

12 The polysuccinimides are prepared by reacting copolymer with  
13 a polyamine to form a mono-, bis-polysuccinimide, higher  
14 polysuccinimide or mixtures thereof. The charge mole ratio  
15 of polyamine to succinic groups in copolymer may determine  
16 the mixture of polysuccinimides formed. For example, a  
17 product comprising mono-, bis-polysuccinimide or higher  
18 polysuccinimide can be prepared by controlling the molar  
19 ratios of the polyamine and succinic groups in copolymer and  
20 the polyamine used. Thus, if about one mole of polyamine is  
21 reacted with one mole of succinic group in the copolymer, a  
22 predominately mono-polysuccinimide product will be prepared.  
23 If about two moles of succinic group in the copolymer are  
24 reacted per mole of polyamine, a bis-polysuccinimide may be  
25 prepared. If higher amounts of succinic group in copolymer  
26 are used, higher polysuccinimides may be prepared provided  
27 that there are sufficient basic amino groups (or sufficient  
28 branching) in the polyamine to react with a succinic group  
29 from each of several copolymer molecules to produce the  
30 higher polysuccinimide. Due to the cross-linking of  
31 copolymer molecules by the polyamine component, compositions  
32 of very high molecular weight, on the order of about 10,000  
33 to about 100,000 may be prepared.

34

01 The reaction of a polyamine with an alkenyl or alkyl  
02 succinic anhydride to produce the polyamino alkenyl or alkyl  
03 succinimides is well known in the art and is disclosed in  
04 U.S. Patents Nos. 2,992,708; 3,018,291; 3,024,237;  
05 3,100,673; 3,219,666; 3,172,892; and 3,272,746. The above  
06 are incorporated herein by reference for their disclosures  
07 of preparing alkenyl or alkyl succinimides. The present  
08 polysuccinimides may be prepared by following the general  
09 procedures described therein.

10  
11 Accordingly, polyamine and copolymer are contacted at the  
12 desired molar ratio to give the desired mono-, bispoly-  
13 succinimides or higher polysuccinimides or mixtures thereof.  
14 The reaction may be carried out neat or preferably in  
15 solution. Suitable solvents include organic solvents,  
16 including alcohols, aliphatic and aromatic solvents, and the  
17 like. The reaction is conducted at a temperature of about  
18 80°C to about 250°C, preferably from about 120°C to about  
19 180°C and is generally complete within about 2 to about 24  
20 hours. The reaction may be conducted under ambient pressure  
21 and atmospheric conditions, although a nitrogen atmosphere  
22 at atmospheric pressure may be preferred. The desired  
23 product may be isolated by conventional procedures, such as  
24 water wash and stripping, usually with the aid of vacuum, of  
25 any residual solvent.

26

27 B(4) General Preparation of Preferred Polysuccinimides

28

29 The preferred polysuccinimides of the present invention are  
30 prepared by reacting a polyPIBSA copolymer of the present  
31 invention with polyamine. The charge mole ratio of  
32 polyamine to succinic groups in the polyPIBSA will effect  
33 whether monopolysuccinimides, bis-polysuccinimides, or  
34 higher polysuccinimides or mixtures thereof are produced



31

01 and/or predominate. Accordingly, with a charge mole ratio  
02 (CMR) of about one mole of polyamine per mole of succinic  
03 groups in the polyPIBSA primarily mono-polysuccinimide will  
04 be formed. However, at a CMR of 0.5 mole polyamine per mole  
05 of succinic group in the polyPIBSA, there is a tendency to  
06 form bis-polysuccinimides where the polyamine component acts  
07 to link two succinic groups, thusly forming a cross-linked  
08 composition. Accordingly, the reaction of polyPIBSA and  
09 polyamine will yield a mixture of products which I term  
10 "polysuccinimides" and which term includes monopolysuccini-  
11 mides, also higher succinimides and bis-polysuccinimides and  
12 compositions of intermediate structure.

13

14 The reaction is carried out by contacting polyamine and  
15 polyPIBSA. Although the ratio of the reactants is not  
16 critical, as noted above a CMR may be chosen so as to yield  
17 desired polysuccinimide proportions. The reaction is  
18 carried out at a temperature sufficient to cause reaction of  
19 the polyamine with a succinic group of the polyPIBSA. In  
20 particular, reaction temperatures from about 120°C to about  
21 180°C are preferred, with temperatures from about 140°C to  
22 about 170°C being especially preferred.

23

24 The reaction may be conducted neat - that is both the  
25 polyamine and the polyPIBSA are combined and then stirred at  
26 the reaction temperature.

27

28 Alternatively, the reaction may be conducted in a diluent.  
29 For example, the reactants may be combined in a solvent such  
30 as aliphatic or aromatic solvents, and the like, and then  
31 stirred at the reaction temperature. After completion of  
32 the reaction, volatile components may be stripped off. When

33

34

32

01 a diluent is employed, it is preferably inert to the reac-  
02 tants and products formed and is generally used in an amount  
03 sufficient to ensure efficient stirring.  
04

05 Preferred are polyamines having from about 2 to about 12  
06 amine nitrogen atoms and from about 2 to about 40 carbon  
07 atoms. The more preferred polyamines employed in this  
08 reaction are generally represented by the formula:  
09



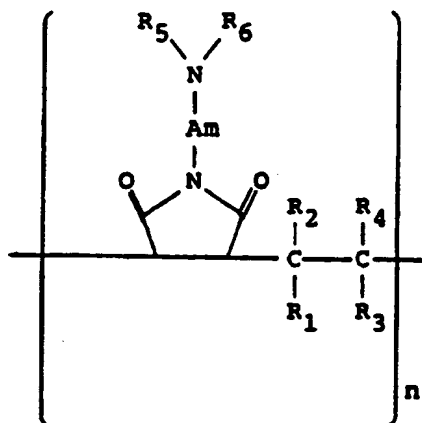
12 wherein Y is an alkylene group of 2 to 10 carbon atoms,  
13 preferably from 2 to 6 carbon atoms, and a is an integer  
14 from about 1 to 11, preferably from 1 to 6. However, the  
15 preparation of these alkylene polyamines does not produce a  
16 single compound and cyclic heterocycles, such as piperazine,  
17 may be included to some extent in the alkylene diamines.  
18

19 B(5) Preferred Polysuccinimides  
20

21 (a) Monopolysuccinimides  
22

23 Preferred monopolysuccinimides include those having the  
24 following formula:  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34

33



wherein Am is a linking group having from about 0 to about 10 amine nitrogen atoms and from about 2 to about 40 carbon atoms; n is 1 or greater and  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are selected from hydrogen lower alkyl of 1 to 6 carbon atoms; and high molecular weight polyalkyl; wherein either  $R_1$  and  $R_2$  are hydrogen and one of  $R_3$  and  $R_4$  is lower alkyl and the other is high molecular weight polyalkyl or  $R_3$  and  $R_4$  are hydrogen and one of  $R_1$  and  $R_2$  is lower alkyl and the other is high molecular weight polyalkyl; and  $R_5$  and  $R_6$  are independently hydrogen, lower alkyl of 1 to 6 carbon atoms, phenyl or taken together are alkylene of 3 to 6 carbon atoms to give a ring.

Preferred high molecular weight polyalkyl groups include polyisobutyl groups having at least about 30 carbon atoms, more preferably, at least about 50 carbon atoms. Especially preferred are polyisobutyl groups having an average molecular weight of about 500 to about 5000, more preferably from about 900 to about 2500.

34

01 Preferred lower alkyl groups include methyl and ethyl.  
02 Especially preferred are compounds where the lower alkyl  
03 group is methyl.  
04  
05 Preferred are compounds where  $R_5$  and  $R_6$  are hydrogen or  
06 methyl; preferred  $R_5$  and  $R_6$  groups include hydrogen.  
07  
08 Preferred are Am groups having from about 0 to about 10  
09 amine nitrogen atoms and from about 2 to about 40 carbon  
10 atoms. More preferred are Am groups of the formula  
11  $-[(ZNH)_pZ']-$  wherein Z and Z' are independently alkylene of  
12 from about 2 to about 6 carbon atoms and p is an integer  
13 from 1 to 6. Especially preferred are Am groups where Z and  
14 Z' are ethylene and p is 2, 3 or 4.  
15  
16 Preferred are compounds where n is from about 2 to about 20,  
17 more preferably from about 2 to about 10.  
18  
19 Preferred are compounds having an average degree of polymer-  
20 ization of from about 1.1 to about 20, more preferably from  
21 about 1.5 to about 10.

22  
23 (b) Bis-polysuccinimides

24  
25 Preferred polysuccinimides include those which partially  
26 comprise at least in part a bis-polysuccinimide structure.  
27 Some of these preferred polysuccinimides are random poly-  
28 succinimides which comprise units selected from:  
29  
30  
31  
32  
33  
34

35

01

02

03

04

05

06

07

08

09

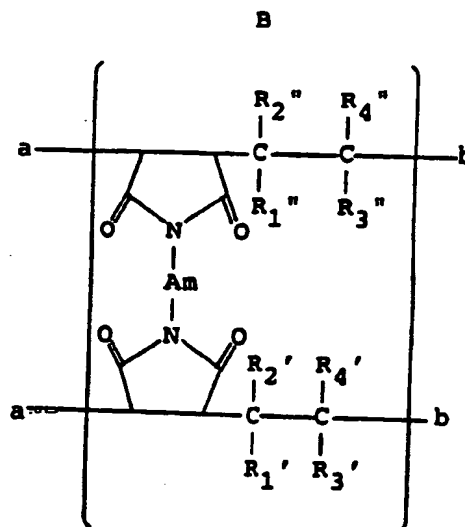
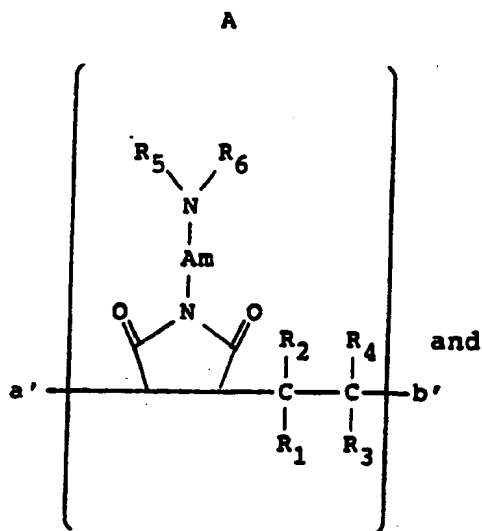
10

11

12

13

14



15 wherein Am is a linking group having from about 0 to 10  
 16 amine nitrogen atoms and from about 2 to 40 carbon atoms;  
 17  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_1'$ ,  $R_2'$ ,  $R_3'$ ,  $R_4'$ ,  $R_1''$ ,  $R_2''$ ,  $R_3''$ , and  $R_4''$   
 18 are selected from hydrogen, lower alkyl of one to 6 carbon  
 19 atoms and high molecular weight polyalkyl; wherein either  $R_1$   
 20 and  $R_2$  are hydrogen and one of  $R_3$  and  $R_4$  is lower alkyl and  
 21 the other is polyalkyl, or  $R_3$  and  $R_4$  are hydrogen and one of  
 22  $R_1$  and  $R_2$  is lower alkyl and the other is polyalkyl; either  
 23  $R_1'$  and  $R_2'$  are hydrogen and one of  $R_3'$  and  $R_4'$  is lower  
 24 alkyl and the other is polyalkyl, or  $R_3'$  and  $R_4'$  are  
 25 hydrogen and one of  $R_1'$  and  $R_2'$  is lower alkyl and the other  
 26 is polyalkyl; and either  $R_1''$  and  $R_2''$  are hydrogen and one of  
 27  $R_3''$  and  $R_4''$  is lower alkyl and the other is polyalkyl or  $R_3''$   
 28 and  $R_4''$  are hydrogen and one of  $R_1''$  and  $R_2''$  is lower alkyl  
 29 and the other is polyalkyl and  $R_5$  and  $R_6$  are independently  
 30 hydrogen, lower alkyl of 1 to 6 carbon atoms, phenyl or  
 31 taken together are alkylene of 3 to 6 carbon atoms to give a  
 32 ring; a, a', b and b' are sites for a covalent bond provided  
 33 that at least one a or a' site of each unit is covalently  
 34 bonded to a b or b' site.

01 Preferred polyalkyl groups include polyisobutyl groups  
02 having at least about 30 carbon atoms, more preferably at  
03 least about 50 carbon atoms. Especially preferred are  
04 polyisobutyl groups having an average molecular weight of  
05 about 500 to about 5000, more preferably from about 900 to  
06 about 2500.

07

08 Preferred lower alkyl groups include methyl and ethyl;  
09 especially preferred is ethyl.

10

11 Preferred Am groups include those having the formula  
12  $\{(\text{ZNH})\text{pZ}'\}$ — wherein Z and Z' are independently alkylene of 2  
13 to 6 carbon atoms and p is an integer from 0 to 5.  
14 Especially preferred are Am groups wherein Z and Z' are  
15 ethylene and p is 1, 2 or 3.

16

17 Preferred are random polysuccinimides where the average sum  
18 of A and B units is from about 2 to about 50. preferred are  
19 random polysuccinimides having molecular weights of from  
20 about 10,000 to about 150,000.

21

22 Preferred are compounds in which the bis-succinimide  
23 structure predominates, that is those having more B units  
24 than A units, preferably on the order of about 2 to about 10  
25 times as many B units as A units. Such compounds are  
26 preferred in part due to their high average molecular  
27 weights, on the order of about 10,000 to about 150,000 which  
28 may be related to their exhibiting an advantageous V.I.  
29 credit as well as dispersantability when used in a  
30 lubricating oil composition.

31

32 It is believed that polysuccinimide compounds in which a  
33 significant portion comprises a bis-polysuccinimide  
34 structure (an embodiment which is exemplified in FIG. 1)

01 comprise network or ladder polymers. Such polymers are  
02 cross-linked in an orderly manner. It is believed that this  
03 orderly cross-linking allows for the formation of composi-  
04 tions having very high molecular weights, on the order of  
05 about 10,000 to about 150,000 and also contributes to the  
06 advantageous properties of these compositions including  
07 improved dispersancy and V.I. credit. In addition, due to  
08 the cross-linking of the copolymer molecules by the poly-  
09 amine to form the polysuccinimides of the above-noted  
10 structure, such products are harder to hydrolyze and are  
11 more stable to shear forces than are those polysuccinimides  
12 which do not form the ladder structure.

13  
14 (c) Higher Polysuccinimides  
15

16 Higher polysuccinimides are prepared by reacting the copoly-  
17 mers of the present invention with a polyamine having  
18 branching such that it can react with a succinic group from  
19 each of greater than two copolymer molecules. Due to this  
20 crosslinking, it is believed that these higher polysucci-  
21 nimides may have gel-like properties besides the dispersant  
22 properties possessed by the other polysuccinimides.

23  
24 C. POLYAMINO POLYSUCCINIMIDES WHEREIN ONE  
25 OR MORE OF THE NITROGENS IS SUBSTITUTED  
26 WITH HYDROCARBYL OXYCARBONYL, HYDROXY HYDROCARBYL  
27 OXYCARBONYL, OR HYDROXY POLY(OXYALKYLENE)OXYCARBONYL)  
OR THE POLYSUCCINIMIDE IS OTHERWISE POST-TREATED

28 Commonly-assigned U.S. Patent No. 4,612,132 discloses poly-  
29 amino alkenyl or alkyl succinimides wherein one or more of  
30 the nitrogens of the polyamino moiety is substituted with a  
31 hydrocarbyl oxycarbonyl, or a hydroxy hydrocarbyl oxycar-  
32 bonyl wherein said hydrocarbyl contains from 1 to about 20  
33 carbon atoms and said hydroxy hydrocarbyl contains from  
34 about 2 to about 20 carbon atoms which may be prepared by

38

01 reaction with a cyclic carbonate; by reaction with a linear  
02 mono- or polycarbonate; or by reaction with a suitable  
03 chloroformate and hydroxy poly(oxyalkylene)oxycarbonyl which  
04 may be formed by reaction with a suitable chloroformate.  
05 U.S. Patent No. 4,612,132 also discloses processes for the  
06 preparation of such modified polyamino alkenyl or alkyl  
07 succinimides.

08

09 U.S. Patent No. 4,612,132 also discloses the post-treating  
10 of hydroxyhydrocarbyl carbamates prepared from polyamino  
11 alkenyl or alkyl succinimides with an alkenyl or alkyl  
12 succinic anhydride.

13

14 In addition, U.S. Patent No. 4,612,132 discloses the reac-  
15 tion of the modified succinimides disclosed therein with  
16 boric acid or similar boron compound to give borated  
17 dispersants. Accordingly, the disclosure of U.S. Patent  
18 No. 4,612,132 is incorporated herein by reference.

19

20 Commonly assigned U.S. Patent No. 4,585,566 discloses  
21 improved dispersants prepared by reacting other  
22 nitrogen-containing dispersants with cyclic carbonates, the  
23 disclosure of which is incorporated herein by reference.

24

25 Accordingly, by following the procedures disclosed in U.S.  
26 Patents Nos. 4,612,132 and 4,585,566, modified polysuccini-  
27 mides may be prepared. Thus, the polyamino polysuccinimides  
28 wherein one or more of the nitrogens of the polyamino moiety  
29 is substituted with a hydrocarbyl oxycarbonyl, or a hydroxy  
30 hydrocarbyl oxycarbonyl wherein said hydrocarbyl contains  
31 from 1 to about 20 carbon atoms and said hydroxy hydrocarbyl  
32 contains from 2 to about 20 carbon atoms may be prepared by  
33 reaction with a cyclic carbonate; by reaction with a linear  
34 mono- or poly-carbonate; or by reaction with a suitable



39

01 chloroformate. Hydroxy poly(oxyalkylene) oxycarbonyl may be  
02 formed by reaction with a suitable chloroformate. Also,  
03 hydroxy hydrocarbyl carbamates prepared from the polysuccinimides of the present invention may be post-treated with an  
04 alkenyl or alkyl succinic anhydride (or even the copolymers  
05 of the present invention (such as polyPIBSA) according to  
06 the procedures disclosed in U.S. Patents Nos. 4,612,132 and  
07 4,585,566. The products so produced are effective disper-  
08 sant and detergent additives for lubricating oils and for  
09 fuel.  
10

11

12 The polysuccinimides and modified polysuccinimides of this  
13 invention can also be reacted with boric acid or a similar  
14 boron compound to form borated dispersants having utility  
15 within the scope of this invention. In addition to boric  
16 acid (boron acid), examples of suitable boron compounds  
17 include boron oxides, boron halides and esters of boric  
18 acid. Generally from about 0.1 equivalents to 10 equiva-  
19 lents of boron compound to the polysuccinimide or modified  
20 polysuccinimide may be employed.

21

22 Commonly-assigned U.S. Patent No. 4,615,826 discloses the  
23 treating of a succinimide having at least one basic nitrogen  
24 with a fluorophosphoric acid or ammonium salt thereof to  
25 give a hydrocarbon-soluble fluorophosphoric acid adduct..  
26 Accordingly, the disclosure of U.S. Patent No. 4,615,826 is  
27 incorporated herein by reference.

28

29 By following the disclosure of U.S. Patent No. 4,615,826,  
30 hydrocarbon-soluble fluorophosphoric adducts of the poly-  
31 succinimides of the present invention may be prepared. Such  
32 adducts comprise the reaction product of a polysuccinimide  
33 of the present invention and a fluorophosphoric acid or  
34

40

01 ammonium salt thereof wherein the amount of said fluoro-  
02 phosphoric acid or salt thereof is from about 0.1 to about 1  
03 equivalent per equivalent of basic nitrogen atom.

04

05 The copolymers of the present invention, including preferred  
06 copolymers such as polyPIBSA may be post-treated with a wide  
07 variety of other post-treating reagents. U.S. Patent  
08 No. 4,234,435, the disclosure of which is incorporated  
09 herein by reference, discloses reacting succinic acylating  
10 agents with a variety of reagents to give post-treated  
11 carboxylic acid derivative compositions which are useful in  
12 lubricating oil compositions.

13

14

#### D. LUBRICATING OIL COMPOSITIONS

15

16 The copolymers, polysuccinimides and modified polysuccini-  
17 mides of this invention are useful as detergent and disper-  
18 sant additives when employed in lubricating oils. When  
19 employed in this manner, the additives of the present  
20 invention are usually present in from 0.2 to 10 percent by  
21 weight to the total composition and preferably at about 0.5  
22 to 8 percent by weight and more preferably at about 1 to  
23 about 6 percent by weight. The lubricating oil used with  
24 the additive compositions of this invention may be mineral  
25 oil or synthetic oils of lubricating viscosity and prefer-  
26 ably suitable for use in the crankcase of an internal  
27 combustion engine. Crankcase lubricating oils ordinarily  
28 have a viscosity of about 1300 CSt 0°F to 22.7 CSt at 210°F  
29 (99°C). The lubricating oils may be derived from synthetic  
30 or natural sources. Mineral oil for use as the base oil in  
31 this invention includes paraffinic, naphthenic and other  
32 oils that are ordinarily used in lubricating oil composi-  
33 tions. Synthetic oils include both hydrocarbon synthetic  
34 oils and synthetic esters. Useful synthetic hydrocarbon

41

01 oils include liquid polymers of alpha olefins having the  
02 proper viscosity. Especially useful are the hydrogenated  
03 liquid oligomers of  $C_6$  to  $C_{12}$  alpha olefins such as 1-decene  
04 trimer. Likewise, alkyl benzenes of proper viscosity, such  
05 as didodecyl benzene, can be used.

06

07 Blends of hydrocarbon oils with synthetic oils are also  
08 useful. For example, blends of 10 to 25 weight percent  
09 hydrogenated 1-decene trimer with 75 to 90 weight percent  
10 150 SUS (100°F) mineral oil gives an excellent lubricating  
11 oil base.

12

13 Lubricating oil concentrates are also included within the  
14 scope of this invention. The concentrates of this invention  
15 usually include from about 90 to 10 weight percent, prefer-  
16 ably from about 90 to about 50 weight percent, of an oil of  
17 lubricating viscosity and from about 10 to 90 weight per-  
18 cent, preferably from about 10 to about 50 weight percent,  
19 of an additive of this invention. Typically, the concen-  
20 trates contain sufficient diluent to make them easy to  
21 handle during shipping and storage. Suitable diluents for  
22 the concentrates include any inert diluent, preferably an  
23 oil of lubricating viscosity, so that the concentrate may be  
24 readily mixed with lubricating oils to prepare lubricating  
25 oil compositions. Suitable lubricating oils which can be  
26 used as diluents typically have viscosities in the range  
27 from about 35 to about 500 Saybolt Universal Seconds (SUS)  
28 at 100°F (38°C), although an oil of lubricating viscosity  
29 may be used.

30

31 Other additives which may be present in the formulation  
32 include rust inhibitors, foam inhibitors, corrosion  
33 inhibitors, metal deactivators, pour point depressants,  
34 antioxidants, and a variety of other well-known additives.

42

01 It is also contemplated the additives of this invention may  
02 be employed as dispersants and detergents in hydraulic  
03 fluids, marine crankcase lubricants and the like. When so  
04 employed, the additive is added at from about 0.1 to 10  
05 percent by weight to the oil. Preferably, at from 0.5 to 8  
06 weight percent.

07

08

#### E. FUEL COMPOSITIONS

09

10 When used in fuels, the proper concentration of the additive  
11 necessary in order to achieve the desired detergency is  
12 dependent upon a variety of factors including the type of  
13 fuel used, the presence of other detergents or dispersants  
14 or other additives, etc. Generally, however, and in the  
15 preferred embodiment, the range of concentration of the  
16 additive in the base fuel is 10 to 10,000 weight parts per  
17 million, preferably from 30 to 5000 parts per million of the  
18 additive per part of base fuel. If other detergents are  
19 present, a lesser amount of the additive may be used.  
20 The additives of this invention may be formulated as a fuel  
21 concentrate, using an inert stable oleophilic organic  
22 solvent boiling in the range of about 150° to 400°F.  
23 Preferably, an aliphatic or an aromatic hydrocarbon solvent  
24 is used, such as benzene, toluene, xylene or higher-boiling  
25 aromatics or aromatic thinners. Aliphatic alcohols of about  
26 3 to 8 carbon atoms, such as isopropanol, isobutylcarbinol,  
27 n-butanol and the like, in combination with hydrocarbon  
28 solvents are also suitable for use with the fuel additive.  
29 In the fuel concentrate, the amount of the additive will be  
30 ordinarily at least 5 percent by weight and generally not  
31 exceed 70 percent by weight, preferably from 5 to 50 and  
32 more preferably from 10 to 25 weight percent.

33

34

43

01 The following examples are offered to specifically  
02 illustrate this invention. These examples and illustrations  
03 are not to be construed in any way limiting the scope of  
04 this invention.

05

06

EXAMPLES

07

Example 1

08

09

Preparation of Polyisobutyl-24 PolyPIBSA

10

11 To a 12-liter, 3-neck flask equipped with an overhead  
12 stirrer, thermometer, condenser, and heating mantle under  
13 nitrogen atmosphere was added 5,000 grams (5.265 mole) of  
14 polyisobutene of about 950 molecular weight having the trade-  
15 name ULTRAVIS-10 obtained from BP Chemicals wherein the  
16 methylvinylidene isomer comprised about 70% of the total  
17 composition, 1547.1 grams (15.79 mole) maleic anhydride, and  
18 2,500 ml chloroform. The mixture was heated to reflux, and  
19 to this was added 67.21 grams (0.41 mole) 22'-azobis  
20 (2-methyl-propionitrile) ("AIBN"). The mixture was refluxed  
21 for two hours at which time an additional 67.21 grams of  
22 AIBN was added. This was followed by another two hours of  
23 reflux and a third charge (66.58 grams) of AIBN. A total of  
24 201 grams (1.2 mole) of AIBN was added. The reaction  
25 mixture was refluxed a total of 20 hours, and then allowed  
26 to cool. Two layers formed. The lower phase which  
27 contained mostly chloroform and unreacted maleic anhydride  
28 was discarded. The upper layer which contained mainly  
29 product and unreacted polyisobutene was separated. Solvent  
30 and maleic anhydride were removed in vacuo. A total of  
31 4,360 grams of product having a saponification number of  
32 40.4 was recovered.

33

34

44

01

Example 2

02

Preparation of Polyisobutyl-24 PolyPIBSA

03

04 To a 1-liter 3-neck flask equipped with a thermometer,  
05 overhead stirrer, nitrogen inlet and water condenser, was  
06 added 165.02 grams (0.174 mole) polyisobutylene (ULTRAVIS-10  
07 from BP Chemicals) and 105 ml dichloroethane, then  
08 16.4 grams (0.167 mole) maleic anhydride were added. The  
09 resulting mixture was heated to about 45°C, and 3.3 grams  
10 (0.017 mole) tert-butylperbenzoate was added. The resulting  
11 mixture was heated to reflux (83°C). The reaction mixture  
12 was heated (with stirring) for a total of 30 hours. The  
13 reaction mixture was allowed to cool. The solvent was  
14 removed in vacuo. Unreacted maleic anhydride was removed by  
15 heating the residue to 150°C at 0.1 mm Hg vacuum. A total  
16 of 176.0 grams product was obtained, which had an average  
17 molecular weight of about 5000. The conversion was about  
18 60%. The saponification number was 73.3.

19

Examples 3 to 15 and Comparison Examples 1C to 5C

21

22 Table I tabulates additional preparations following the  
23 basic synthetic procedure outlined in Examples 1 and 2.  
24 Table I lists the reactants, reaction temperature, time and  
25 solvent, and free radical initiator used.

26

27 Example 12 was prepared using polyisobutene of about 1300  
28 molecular weight having the trade name ULTRAVIS-30 obtained  
29 from BP chemicals wherein the methylvinylidene isomer  
30 comprised about 70% of the total composition.

31

32 Comparison Examples 1C to 5C were prepared using a  
33 polyisobutylene of about 950 molecular weight prepared with  
34

45

01 AlCl<sub>3</sub> catalysis having the trade name Parapol 950 obtained  
 02 from Exxon Chemical.

03

04

05

TABLE I

06

07 Product

08 of

09 Example

No.

Polybutene  
(g)Maleic  
Anhydride  
(g)Solvent  
(ml)Initiator\*  
(g)Temp  
°CTime  
Hrs.

10	2	Ultravis-10 (165.09)	16.4	Dichloroethane (105)	TBPP (3.3)	83	30
11							
12	3	Ultravis-10 (384.6)	119	Toluene (250)	AIBN (15.5)	110	6
13							
14	4	Ultravis-10 (330)	32.3	Chlorobenzene (210)	DTBP (5.8)	138	30
15							
16	5	Ultravis-10 (5000)	1547	Dichloroethane (2500)	AIBN (200)	83	13
17							
18	6	Ultravis-10 (384.6)	119	Chloroform (250)	AIBN (15.5)	74	24
19							
20	7	Ultravis-10 (384.6)	119	Methylene Chloride (250)	AIBN (15.5)	40	94
21							
22	8	Ultravis-10 (330)	32.3	Toluene (210)	DTBP (5.8)	110	30
23							
24	9	Ultravis-10 (330)	32.3	Xylene (210)	DTBP (5.8)	144	39
25							
26	10	Ultravis-10 (330)	32.3	Xylene (210)	DTBP (5.8)	114	4
27							
28	11	Ultravis-10 (330)	32.3	Toluene (210)	DTBP (5.8)	110	4
29							
30							
31	12	Ultravis-30 (217.1)	16.4	Dichloroethane (105)	TBPP (3.3)	83-184	26
32							
33	13	Ultravis-10 (3350)	328.3	Chlorobenzene (1600)	DTBP (42.6)	138	28
34							

46

TABLE I (Cont'd)

Product of Example No.	Polybutene (g)	Maleic Anhydride (g)	Solvent (ml)	Initiator* (g)	Temp °C	Time Hrs.
14	Ultravis-10 (5000)	515.8	Chloroform (3000)	TBPB (102.8)	72	54
15	Ultravis-10 (10,000)	1031	Chloroform (6000)	TBPB (205.6)	72 then 140	48 2
1C	Parapol 950 (384.6)	119	Toluene (250)	AIBN (15.5)	110	6
2C	Parapol 950 (76.4)	23.8	Dichloroethane (50)	AIBN (2.33)	83	4
3C	Parapol 950 (330)	32.3	Toluene (210)	DTBP (5.8)	110	30
4C	Parapol 950 (330)	32.3	Xylene (210)	DTBP (5.8)	114	30
5C	Parapol 950 (330)	32.3	Chlorobenzene (210)	DTBP (5.8)	138	30

\* AIBN = 2,2'-azobis (2-methyl-propionitrile); DTBP = di-tert-butyl peroxide; TBPB = tert-butyl peroxybenzoate

\*\* Molecular weight 1300

Example 16

A 500-ml, 3-necked flask was charged with 100g of a polyPIBSA polybutene mixture (prepared according to the method of Example 5) which comprised about 38 weight percent polyPIBSA and about 62 weight percent unreacted polyisobutene (of which about 68 weight percent comprised the methylvinylidene isomer). The mixture was heated to 70°C. Then, 8g maleic anhydride and 1.7g di-tert-butyl peroxide were added to the mixture. The mixture was stirred and



47

01 heated to 150°C for 5 hours. After allowing the mixture to  
02 cool, 150 ml hexane was added to precipitate unreacted  
03 maleic anhydride which was then removed by filtration. The  
04 hexane was removed by stripping for 4 hours at 36 mm Hg  
05 (abs) at 90°C. The product had a maleic anhydride content  
06 of 0.08 weight percent.

07

08

Example 17A

09

10 A 22-liter, 3-necked flask was charged with 3752g of  
11 polyisobutene (BP Ultravis 10) and 2800g of a polyPIBSA  
12 polyisobutene mixture (prepared according to Example 13)  
13 which comprised about 57 weight percent polyPIBSA and about  
14 43 weight percent unreacted polyisobutene). The mixture was  
15 heated to 91°C; then 14g maleic anhydride and 2.7g  
16 di-tert-butyl peroxide (DTBP) were added. A slight exotherm  
17 was noticed where the temperature increased to 147°C. The  
18 mixture was stirred and heated at 140°C for one hour. After  
19 standing at room temperature overnight, the mixture was  
20 heated to 140°C and 378g maleic anhydride and 56.7g of DTBP  
21 were added. The mixture was stirred and heated at 140°C for  
22 6.5 hours. The mixture was allowed to cool to ambient  
23 temperature overnight. The mixture was heated to 80°C and  
24 vacuum was applied at 28 inches Hg (vac); the temperature  
25 was increased to 200°C. The mixture was stripped at 200°C  
26 and 28 inches Hg (vac) for 2 hours to remove unreacted  
27 maleic anhydride.

28

29

Example 17B

30

31 A 22-liter, 3-necked flask was charged with 8040g  
32 polyisobutene (BP Ultravis 10) and 6000g of a  
33 polyPIBSA/polybutene mixture prepared according to  
34 Example 17A. The mixture was heated to 109°C, then 840g

48

01 maleic anhydride and 126g DTBP were added. The resulting  
02 mixture was stirred and heated at 140°C for 5.25 hours. The  
03 mixture was cooled to ambient temperature. The mixture was  
04 then heated to 128°C with stirring and an additional 153g  
05 maleic anhydride and 23g DTBP were added. The mixture was  
06 stirred and heated at 140°C for 3.5 hours and then an  
07 additional 153g maleic anhydride and 11.8g DTBP were added.  
08 The mixture was stirred and heated at 140°C for an  
09 additional 3.67 hours. The mixture was cooled to ambient  
10 temperature. The mixture was then stirred and heated at  
11 186°C for one hour while vacuum was applied to strip the  
12 unreacted maleic anhydride from the product. The product  
13 had a saponification number of 85.8 mg KOH/g.

14

15

Example 18

16

17

## Preparation of PolyPIBSA TETA

18

Polysuccinimide with a High Degree of Polymerization

19

20 To a 12-liter flask equipped with a Dean Stark trap,  
21 overhead stirrer and heating mantle under nitrogen was added  
22 4340 g polyPIBSA prepared according to Example 1  
23 (saponification No. 40.4 mg KOH/g, molecular weight about  
24 9000). The resulting mixture was heated to 130°C with  
25 stirring, then 163.7g (1.12 mole) triethylenetetraamine  
26 (TETA) were added. The reaction mixture was stirred  
27 overnight at 160°C to 215°C; 24 ml water were collected (in  
28 the Dean Stark trap) The reaction mixture was allowed to  
29 cool.

30

31 Obtained was 4360 g of a polysuccinimide of about 58,000  
32 molecular weight having the following characteristics:  
33 1.45%N, TAN 1.01, TBN 26.9, viscosity at 100°C 2649 cSt.  
34 The molecular weight was determined using 1-1000Å and 1-500Å

49

01 ultrastrogel columns connected in series using 10%  
02 propylamine 90% THF as a solvent and comparing the retention  
03 time with known (molecular weight) polystyrene standards.

04

05

Example 19

06

07

08

Preparation PolyPIBSA TEPA  
Polysuccinimide With a High Degree of Polymerization

09 To a 3-neck one-liter flask equipped with heating mantle,  
10 overhead stirrer and Dean Stark trap, was added 213.4 g  
11 polyPIBSA prepared according to the method of Example 5  
12 (molecular weight about 6000). The system was heated to  
13 90°C with stirring; then 18.98 g of tetraethylene pentaamine  
14 (TEPA) (0.1003 g). The resulting mixture was heated to  
15 176°C under nitrogen sweep. A small amount of water (about  
16 0.5 ml) was removed. After 3.5 hours, the mixture was  
17 placed under vacuum and was heated under vacuum for 0.5  
18 hours; the heating was then stopped. Obtained was 226.9 g  
19 of product, a polyPIBSA TEPA polysuccinimide.

20

21

Example 20

22

23

24

Preparation of PolyPIBSA TETA  
Polysuccinimide With a High Degree of Polymerization

25 To a 12-liter flask equipped with an overhead stirrer,  
26 heating mantle and Dean Stark trap, under nitrogen sweep,  
27 was added 4539 g polyPIBSA prepared according to Example 5  
28 (saponification number 36.3, molecular weight about 6600).  
29 The system was heated to 125°C with stirring; then 131.6 g  
30 triethylene tetraamine (TETA) was added. The reaction  
31 mixture was heated to 165°C for 5 hours. A total of 21.5 ml  
32 water was collected in the Dean Stark trap. The mixture was  
33 then heated under vacuum at 180°C for two hours. The  
34 reaction mixture was allowed to cool. Obtained was 4589 g

50

01 of product, a polysuccinimide of about 35,000 molecular  
02 weight having the following characteristics: %N 1.14, TAN  
03 2.33, TBN 20.1, viscosity at 100°C 1817 cSt.

04

05

Example 21

06

07

## Preparation of PolyPIBSA TETA

08

Polysuccinimide with a Low Degree of Polymerization

09 To a 5-liter flask equipped with a heating mantle, overhead  
10 stirrer and Dean Stark trap under nitrogen sweep, was added  
11 1000 g polyPIBSA prepared according to Example 17B  
12 (saponification number 85.8, molecular weight about 2500)  
13 and 999 g Chevron 100NR diluent oil. The mixture was heated  
14 to 60°C; then 75.78 g TETA was added. The mixture was  
15 heated to 160°C and kept at temperature for 4 hours. A  
16 total of 7.0 ml water was recovered from the Dean Stark  
17 trap. The reaction mixture was then maintained at 160°C  
18 under vacuum for 2 hours. The reaction mixture was allowed  
19 to cool. Obtained was 2018.2 g of product having %N=1.35.

20

21

Example 22

22

23

## Preparation of PolyPIBSA HPA

24

Polysuccinimide With a Low Degree of Polymerization

25 To a 5-liter flask equipped with a heating mantle, overhead  
26 stirrer and Dean Stark trap (under nitrogen sweep) was added  
27 1000 g polyPIBSA prepared according to Example 17B  
28 (saponification number 85.8 molecular weight 2500) and 932  
29 Chevron 100NR diluent oil. The mixture was heated to 60°C;  
30 to this was added 142.45 g heavy polyamine ("HPA") No. X  
31 obtained from Union Carbide Corporation. The mixture became  
32 very thick. The reaction mixture was heated to 165°C and  
33 maintained at that temperature for 4 hours; the mixture  
34 became less viscous. Then the reaction mixture was heated

57

01 at 165°C under vacuum for 2 hours. The mixture was allowed  
02 to cool. Obtained was the above-identified product having  
03 %N=2.23.

04

05

Example A

06

07

Determination of Saponification Number

08

09 Saponification number was determined by using ASTM procedure  
10 D94-80.

11

12 Results for the products of Examples 2 to 15 and 1C to 5C  
13 are given in Table II.

14

15

Example B

16

17

Determination of Percent

18

Unreacted Polyisobutylene and Percent Product

19

20 The percent of unreacted polyisobutylene and percent product  
21 were determined according to the following procedure.

22

23 A 5.0-gram sample of product was dissolved in hexane, placed  
24 in a column of 80.0-gram silica gel (Davisil 62,140Å pore  
25 size silica gel), and eluted with 600 ml hexane. The  
26 percent unreacted polybutylene was determined by removing  
27 the hexane solvent in vacuo (from the eluent) and weighing  
28 the residue. The silica gel from the column was removed and  
29 suspended in a 1-liter beaker with 250 ml dioxane. The  
30 mixture was heated to boiling, and the filtered. The  
31 process was repeated three more times. The dioxane  
32 solutions were combined and then stripped to dryness in  
33 vacuo and the percent product determined by weighing the  
34 residue.

52

01 Results for the Products of Examples 2 to 15 and 1C to 5C  
02 are tabulated in Table II.

03

04 Example C

05

06 Determination of Molecular Weight of  
07 The PolyPIBSA Product and Degree of Polymerization

08

09 The molecular weight of the product was determined according  
10 to the following procedure.

11

12 A 0.5% solution of product in tetrahydrofuran was injected  
13 onto two 500-Å gel permeation columns (ultrastrogel)  
14 connected in series. The solvent used was 1 to 3 percent  
15 methanol in tetrahydrofuran. (The columns were eluted with  
16 a 1% or 3 percent solutions methanol in tetrahydrofuran.)  
17 Molecular weight was determined by comparison of retention  
18 times of the product to the retention times of polystyrene  
19 standards.

20

21 Degree of polymerization was calculated by dividing the  
22 molecular weight by 1,050 (the calculated average molecular  
23 weight of a monomer having one succinic group and one  
24 polyisobutylene group of average molecular weight of 952).

25

26 Results for the products of Examples 2 to 15 and 1C to 5C  
27 are tabulated in Table II.

28

29 Example D

30 Calculation of "PIBSA Number"

31

32 The PIBSA number was calculated by dividing the  
33 saponification number by the percent product. This gave the  
34 "PIBSA number" which is a saponification number for

53

01 polyPIBSA on a 100% actives basis. This value is tabulated  
02 in Table III.

03

04 Calculated PIBSA numbers for the products of Examples 2 to  
05 15 and 1C and 5C are tabulated in Table III.

06

07 It is believed that polyPIBSA comprises a copolymer having  
08 alternating succinic and polyisobutyl groups.

09

10

#### Example E

11

#### Fourier Transform Infrared Spectra of PolyPIBSA

13

14 The Fourier Transform Infrared (FTIR) Spectra (having a  
15 resolution of  $2\text{ cm}^{-1}$ ) of some of the polyPIBSA copolymers of  
16 the present invention and also some comparison compounds  
17 were recorded on a Nicolet MX-1 FTIR. Samples whose spectra  
18 was to be run were prepared by dissolving in Chevron 100NR  
19 mineral oil at a concentration of 5 percent by weight. The  
20 FTIR frequency for the anhydride stretch for each sample was  
21 measured and is recorded in Table IV.

22

23 As may be seen from Table IV, PIBSA prepared by the thermal  
24 process ("thermal PIBSA") prepared from (a) BP ultravis  
25 polyisobutene (having about 70% of the total composition in  
26 the methylvinylidene configuration) and (b) Exxon Parapol  
27 polyisobutene both exhibited the anhydride stretch  
28 frequency at  $1793\text{ cm}^{-1}$ . PIBSA prepared according to the  
29 chlorination process ("Chlorination PIBSA") from the Exxon  
30 Parapol polyisobutene had an anhydride stretch frequency at  
31  $1785\text{ cm}^{-1}$ . In contrast, copolymers of the present invention  
32 comprising polyPIBSA (prepared according to Examples 3 to  
33 12) exhibited anhydride stretch frequencies in the range of  
34  $1777\text{ to }1783\text{ cm}^{-1}$ . Comparison Examples 1C to 5C which were

54

01 prepared by reacting the Exxon Parapol polyisobutene (which  
02 did not comprise at least about 20 percent of the alkyl-  
03 vinylidene isomer) under free radical conditions exhibited  
04 anhydride stretch absorbences in the range of 1785 to 1790  
05  $\text{cm}^{-1}$  the range for the conventional PIBSA materials. It is  
06 believed that these differences are due to the 2,3-disubsti-  
07 tution that is present in the one-to-one alternating  
08 copolymers of the present invention.

09

10

#### Example F

11

#### Fourier Transform Infrared Spectra of Polysuccinimides

12

13  
14 The Fourier Transform Infrared (FTIR) spectra of some of the  
15 polysuccinimides of the present invention and also of some  
16 comparison compounds were recorded. Samples were prepared  
17 as described in Example E and the FTIR frequency for the  
18 succinimide stretch for each sample is recorded in Table V.

19

20 As may be seen from Table V, MS-Th, monosuccinimide prepared  
21 from Thermal PIBSA and BS-Th, bis-succinimide prepared from  
22 Thermal PIBSA exhibit the succinimide stretch at 1705.1  $\text{cm}^{-1}$   
23 and 1707.0  $\text{cm}^{-1}$ , respectively. MS-Cl monosuccinimide  
24 prepared from chlorination PIBSA, PS-Cl, a polysuccinimide  
25 prepared from chlorination PIBSA and CS-CL, a commercial  
26 succinimide prepared from chlorination PIBSA, exhibit  
27 succinimide stretches at 1706.2  $\text{cm}^{-1}$ , 1705.1  $\text{cm}^{-1}$  and  
28 1705.1  $\text{cm}^{-1}$ , respectively.

29

30 In contrast, the polysuccinimides of the present invention  
31 exhibit succinimide stretches between about 1697  $\text{cm}^{-1}$  and  
32 about 1703  $\text{cm}^{-1}$ . It is believed that the characteristic  
33 frequency for the succinimide stretch is due to the  
34 disubstitution at the 2- and 3-positions in the



55

01 polysuccinimide structure, similar to the characteristic  
 02 anhydride stretch exhibited by the polyPIBSA copolymers.

03

04

Example G

05

Sequence VE Test - Sludge

06

07 Formulated oils containing a polysuccinimide of the present  
 08 invention prepared according to Example 18 were tested  
 09 according to the Sequence VE Engine Test Procedure (Sequence  
 10 VE Test Procedure, Seventh Draft, May 19, 1988) and evalu-  
 11 ated for sludge. The test formulations were compared with  
 12 two industry reference oils: Reference A, a poor performing  
 13 oil, and Reference B, a good performing oil. Sludge ratings  
 14 of 9 or greater are advantageous and generally considered  
 15 passing. Results are tabulated in Table VI.

16

17

TABLE II

18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34
		Product	Weight	Saponifica-	%	%	Molecular	Average								
		of	Product,	tion	Unreacted	Product	Wt.	Degree								
		Example	g	Value,	Polybutene		Product	of								
				mgKOH/g				Poly-								
				Sample				meriza-								
								tion								
23		2	176	73.3	40	60	5,000	4.8								
24		3	370	N/A	59	39	1,700	1.6								
25		4	355	78.9	36	58	1,350	1.3								
26		5	4,589+	36.3	64	36	6,600	6.3								
27		6	374+	45.4	62	37	9,100	8.7								
28		7	365+	43.3	57	43	11,000	10.5								
29		8	357	78.3	36	60	1,400	1.3								
30		9	364	78.4	40	53	1,200	1.1								
31		10	361	79.8	39	58	1,300	1.2								
32		11	341	35.8	65	32	1,900	1.8								
33		12	232	39.6	35	65	8,000	5.7								
34		13	3,605	80.3	35	57	1,350	1.3								

56

01 TABLE II (Cont'd)

02			Saponifica-				Average
03			tion				Degree
04	Product	Weight	Value,	%	%	Molecular	of
05	of	Product,	mgKOH/g	Unreacted	Product	Wt.	Poly-
06	Example	g	Sample	Polybutene		Product	meriza-
07	14	5,465	N/A	33	65	3,300	3.1
08	15	10,462	N/A	35	63	12,000	11.4
09	1C	352	24.3	87	11	900	0.9
10	2C	68†	N/A	N/A	N/A	N/A	N/A
11	3C	351	87.3	52	34	900	0.9
12	4C	357	80.9	57	34	950	0.9
13	5C	356	N/A	56	32	950	0.9

15 N/A = Not Available

16 † Formed two phases = from upper phase only

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

57

TABLE III

	<u>Product of Example</u>	<u>PIBSA Number of 100% Active Material*</u>	<u>Average Molecular Weight</u>
01			
02			
03			
04			
05			
06	2	122	5,000
07	3	N/A	1,700
08	4	136	1,350
09	5	101	6,600
10	6	123	9,100
11	7	101	11,000
12	8	131	1,400
13	9	148	1,200
14	10	138	1,300
15	11	112	1,900
16	12	61	8,000
17	13	141	1,350
18	14	N/A	3,300
19	15	N/A	12,000
20			
21	1C	219	900
22	2C	N/A	N/A
23	3C	287	900
24	4C	266	950
25	5C	295	950

N/A = Not Available

\*Includes base titration of benzoic acid initiator, where used.

58

TABLE IV

FTIR Spectra of PolyPIBSA

Sample- Product of Example No.	Molecular Weight	FTIR Frequency (cm <sup>-1</sup> )
2	5,000	1779.7
3	1,700	1781.2
4	1,350	1782.8
5	6,600	1778.1
6	9,100	1777.3
7	11,000	1775.8
8	1,400	1781.2
9	1,200	1782.8
10	1,300	1782.8
11	1,900	1780.5
12	8,000	1778.1
13	1,350	N/A
1C	900	1789.8
2C	N/A <sup>a</sup>	1789.1
3C	900	1785.2
4C	950	1787.5
5C	950	1785.9
Thermal PIBSA (BP polyisobutene)		1793.0
Thermal PIBSA (Exxon polyisobutene)		1793.0
Chlorination PIBSA (Exxon polyisobutene)		1785.
Chlorination PIBSA (Commercial Product)		1785.

<sup>a</sup> N/A = not available.

59

TABLE V

FTIR Spectra of Polysuccinimides

07	<u>Sample-Product of Example No.</u>	<u>FTIR Frequency (cm<sup>-1</sup>)</u>
08		
09	18	1697.5
10	19	N/A
11	20	1699.2
12	21	1700.4
13	22	1699.4
14		
15	MS-Th (mono-succinimide-thermal PIBSA)	1705.1
16	BS-Th (bis-succinimide-chlorination PIBSA)	1707.0
17	MS-Cl (mono-succinimide-chlorination PIBSA)	1706.2
18	PS-Cl (polysuccinimide-chlorination PIBSA)	1705.1
19	CS-Cl (commercial succinimide-chlorination PIBSA)	1705.1
20		
21		
22		
23	N/A = not available.	
24		
25		
26		
27		
28		
29		
30		
31		
32		
33		
34		

60

TABLE VI

Sequence VE Engine Test Results - Sludge

<u>Sample 0.1</u>	<u>Rocker Cover Sludge</u>	<u>Average Engine Sludge</u>
Reference A	1.2	3.8
Reference A	1.6	3.3
Reference B	8.6	8.9
Reference B	9.2	9.2
Oil with 3%		
Product of		
Example 18	9.2	9.3
Oil with 6%		
Product of		
Example 18	9.0	9.2

EXAMPLE 23Preparation of Ethylene Carbonate Treated Bis  
TEPA Polysuccinimide with a High Degree of Polymerization

To a 2 liter 3-necked flask equipped with an overhead stirrer, condensor and nitrogen inlet tube was added 677.0 g polyPIBSA, prepared according to Example 33, with a high degree of polymerization and 950 molecular weight polybutene tail (SAP No. 64.4, 0.389 mol). To this was added 267 g Chevron 100N diluent oil. This was then heated to 120°C under nitrogen with stirring and 36.7 g TEPA (0.194 mol) was added rapidly. This was stirred for 4 hours at 160°C. A total of 5.8 cc. water was produced. This produced a

61

01 bisTEPA polysuccinimide with a high degree of polymeri-  
02 zation. Then the temperature was lowered to 80°C and  
03 102.43 g ethylene carbonate was added (1.16 mol). This  
04 amount was required so that two moles of ethylene carbonate  
05 reacted with each basic nitrogen in the bisTEPA poly-  
06 succinimide. The temperature was increased to 160°C for 4  
07 hours. A total of 1004.51 g of product was produced. The  
08 product had the following properties: Acid No. = 0.08 mg  
09 KOH/g; %N = 1.23%; Alkalinity Value = 14.18 mg KOH/g; and  
10 viscosity at 100°C = 901.2 Cst.

11

12

EXAMPLE 24

13

14

Preparation of Ethylene Carbonate Treated Bis TEPA  
Polysuccinimide with a Low Degree of Polymerization

15

16

17 To a 2 liter 3-necked flask equipped with an overhead  
18 stirrer, condensor and nitrogen inlet tube was added 497.0 g  
19 polyPIBSA prepared according to Example 17B with a low  
20 degree of polymerization and 950 molecular weight polybutene  
21 tail (Saponification No. 85.8, 0.38 mol). To this was added  
22 447 g Chevron 100N diluent oil. This was then heated to  
23 120°C under nitrogen with stirring and 35.9 g TEPA (0.19  
24 mol) was added rapidly. This was stirred for 4 hours at  
25 160°C. A total of 5.9 cc. water was produced. This  
26 produced a bisTEPA polysuccinimide with a low degree of  
27 polymerization. Then the temperature was lowered to 80°C  
28 and 100.32 g ethylene carbonate was added (1.14 mol). This  
29 amount was required so that two moles of ethylene carbonate  
30 reacted with each basic nitrogen in the bisTEPA polysucci-  
31 nimide. The temperature was increased to 160°C for 4 hours.  
32 A total of 1030.0 g of product was produced. The product  
33 had the following properties: Alkalinity Value 14.0 mg  
34 KOH/g.

62

EXAMPLE 25Preparation of Borated Bis HPA Polysuccinimide  
with a High Degree of Polymerization

To a 2 liter 3-necked flask equipped with an overhead stirrer, condensor and nitrogen inlet tube was added 864.0 g polyPIBSA made in a manner similar to Example 35, with a high degree of polymerization and 950 molecular weight polybutene tail (Saponification No. 49.0, 0.38 mol). To this was added 121 g Chevron 100N diluent oil. This was then heated to 140°C under nitrogen with stirring and 52.3 g HPA (0.19 mol) was added rapidly. This was stirred for 4 hours at 170°C. A total of 7.5 cc. water was produced. This produced a bisHPA polysuccinimide with a high degree of polymerization. Then the temperature was lowered to 65°C and 50 cc water and 27.09 g boric acid (0.44 mol) was added. This was heated at reflux (102°C) for 2 hours, then the water was removed by distillation. The temperature was then increased to 171°C for 2.5 hours. Then the product was decanted. The product had the following properties: Acid No. = 2.30 mg KOH/g; %N = 1.68%; %Boron = 0.53; and viscosity at 100°C = 1014 Cst. It is anticipated that this borated product will have improved wear properties.

EXAMPLE 26Preparation of Borated Bis TEPA  
Polysuccinimide with a Low Degree of Polymerization

To a 2 liter 3-necked flask equipped with an overhead stirrer, condensor and nitrogen inlet tube was added 500 g polysuccinimide from Example 46. This was then heated to 50°C under nitrogen with stirring and 50 ml water and 28.2 g boric acid (0.45 mol) was added. This was then heated at



63

01 reflux (102°C) for 2 hours. Then the water was distilled  
02 off, and the temperature was increased to 165°C for 1.5  
03 hours. A total of 517.0 g of product was produced. The  
04 product had the following properties: %N = 1.24; viscosity  
05 at 100°C = 312.5 Cst; Acid No. = 24.3 and %B = 1.01%. It is  
06 anticipated that this borated product will have improved  
07 wear properties.

08

09

EXAMPLES 27 to 36

10

11 Table VII includes the results from additional preparations  
12 of polyPIBSA that were carried out using the basic synthetic  
13 procedure outlined in Examples 1 and 2. Table VII lists the  
14 reactants, reaction temperature, time and solvent and free  
15 radical initiator used as well as the weight of product and  
16 the saponification value.

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

TABLE VII

Product of Example No.	Polybutene (g)	Maleic Anhydride (g)	Solvent (ml)	Initiator (g)	Temp. °C	Time hrs	Weight Product (g)	Saponification value mg KOH/g Sample
27	Ultras-10 (330)	32.34	chlorobenzene (210)	TBPB (1.2)	138	30	345	51
28	Ultras-10 (330)	32.34	chlorobenzene (210)	TBPB (0.6)	138	30	331	38
29	Ultras-30 (2171)	164	dichloroethane (1050)	TBPB (33)	83	23	2265	55
30	Ultras-30 (4147)	328	chlorobenzene (1600)	DTBP (42.6)	142	20	4429	67
31	Ultras-30 (4342)	328	dichloroethane (2000)	TBPB (66)	83	22	4633	47
32	Ultras-10 (5000)	515.8	dichloroethane (3000)	DTBP (77.4)	90	42	5506	46
33	Ultras-10 (5000)	515.8	dichloroethane (3000)	DTBP (77.4)	91	92	5339	64.4

TBPB = t-butylperoxybenzoate

DTBP = di-t-butyl peroxide

65

TABLE VII (continued)

Product of Example No.	Polybutene (g)	Maleic Anhydride (g)	Solvent (ml)	Initiator (g)	Temp. °C	Time hrs	Weight Product (g)	Saponification valve mg KOH/g Sample
34	Ultras-30 (5000)	376.9	dichloroethane (3000)	DTBP (56.2)	91	92	5350	34
35	Ultras-10 (2000)	205.88	dichloroethane (1200)	EDTBPB (96.8)	91	29	2100	51
36	Ultras-30 (6000)	453	dichloroethane (3000)	TBPO (149.91)	91	24	6272	50

DTBP = dit-butyl peroxide

TBPO = t-butyl peroxoanoate

EDTBPB = ethyl -3,3-di(t-butyl peroxy)butyrate

66

01

EXAMPLES 37 to 48

02

03 Table VIII includes the results from additional preparations  
04 of polysuccinimides that were carried out using the basic  
05 synthetic procedure outlined in Examples 18-22. Table VIII  
06 lists the polyPIBSA used, the amount of diluent oil added,  
07 the polyamine used, the calculated charge mol ratio (CMR),  
08 the weight of final product, the water produced, and the %N.

09

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

TABLE VIII

Example	PolyPIBSA Used (g)	Diluent Oil (g)	Polyamine Used (g)	CMR	Vt. of Product (g)	XN	ml H <sub>2</sub> O Produced
37	Example 17B (500)	443.9	HPA (93.6)	0.89	1025.7	2.94	6.2
38	Example 17B (1000)	1019	TETA (55.8)	0.5	2122.6	0.99	9.1
39	Example 15 *(1280)	696	TETA (99.3)	0.89	2060	1.79	15.0
40	Example 31 **(1949)	72	TETA (55.8)	0.5	1965.2	0.98	12
41	Example 32 (1776.8)	1881	HPA (104.5)	0.5	3740	0.92	13
42	Example 35 (1423.0)	690	TETA (110.96)	0.89	2200	1.8	16.5
43	Example 35 (1273)	1697	HPA (104.5)	0.5	3060	1.13	14
44	Example 31 (1403.6)	500	HPA (75.21)	0.5	1965	2.14	13
45	Example 36 (500)	109	HPA (28.88)	0.5	606.3	1.50	3.6

\*In this example, extra diluent oil (36%) was added to the polyPIBSA to make it easier to filter.

\*\*In this example, extra diluent oil (18.4%) was added to the polyPIBSA to make it easier to filter.

TABLE VIII (continued)

Example	Polypibsa Used (g)	Diluent Oil (g)	Polyamine Used (g)	CHR	Vt. of Product (g)	ZN	ml H <sub>2</sub> O Produced
46	Example 17B (2500)	2248	TEPA (180.59)	0.5	4879.2	1.4	31
47	Example 35 (458)	26.7	TEPA (18.9)	0.5	501.79	1.2	3.6
48	Example 17B (261.62)	209.11	TEPA (32.89)	0.87%	497.34	2.2	2.6

01  
02  
03  
04  
05  
06  
07  
08  
09  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24

69

01

EXAMPLE 49

02

03

Viton Seal Swell Test

04

05 Some lubricating oil additives have been identified as being  
06 deleterious to fluoroelastomers such as Viton that are  
07 currently used as gasket materials in automobile engines.  
08 European engine builders have now placed fluoroelastomer  
09 seal tests into their engine oil specifications. One such  
10 test is the Volkswagen VW3334 (September 1987) Seal Swell  
11 Test. This procedure is described in the Third Symposium of  
12 the European Coordination Council (CEC) 1989 in an article  
13 entitled "Engine and Bench Aging Effects on the  
14 Compatibility of Fluoroelastomers with Engine Oils" by  
15 Dr. S. W. Harris and J. C. Downey of Amoco Petroleum  
16 Additives Company.

17

18 The VW3334 (September 1987) Seal Swell Test was carried out  
19 on samples of Viton from the Parker Prudifa Company which  
20 were cut into dumbbell shapes, using a formulated  
21 lubricating test oil that contained succinimide dispersant,  
22 overbased detergent, antioxidant and viscosity index  
23 improver materials at a bath temperature of 150°C for a 96  
24 hour immersion time. The immersion procedure was similar to  
25 ASTM D471-79 Standard Test Method for Rubber Property-Effect  
26 of Liquids. Commercial succinimide dispersants were  
27 compared to the polysuccinimides of present Examples 47 and  
28 48. The Viton samples were then subjected to analysis of  
29 their tensile properties using procedures similar to ASTM  
30 D412-87 Standard Test Method for Rubber Properties in  
31 Tension. The properties that were measured were cracking at  
32 120 percent elongation, percent change in tensile strength  
33 and percent change in elongation at break, in accordance

34

01 with the VW3334 Seal Swell Test requirements. The results  
02 are shown in Table IX.

03

04 The data in Table IX demonstrates that the polysuccinimide  
05 of Example 47 passed the Viton Seal Swell Test at the 0.07%  
06 nitrogen level, whereas the commercial bis-succinimide  
07 failed. Although the polysuccinimide of Example 48 did not  
08 pass the Viton test at the 0.13% nitrogen level, it  
09 performed better in this test than the commercial mono-  
10 succinimide at the 0.12% nitrogen level.

11

12

TABLE IX

13

14

VITON SEAL SWELL TEST

15

16	<u>Sample</u>	<u>Ts</u> <sup>1</sup>	<u>El</u> <sup>2</sup>	<u>Cr</u> <sup>3</sup>	<u>%N</u>
17					
18	Commercial monosuccinimide	-54	-43	Yes	0.12
19	Polysuccinimide, Example 48	-49	-39	Yes	0.13
20	Commercial bis-succinimide	-29	-23	No	0.07
21	Polysuccinimide, Example 47	-15	-17	No	0.07
22					
23	passing limit	±20	±25	No	

24

25

26 <sup>1</sup>Tensile strength % change27 <sup>2</sup>Elongation to break % change28 <sup>3</sup>Cracks, yes or no at 120% elongation

29

30

31

32

33

34



01  
02  
03  
04  
05  
06  
07  
08  
09  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34

EXAMPLE 50

This example shows that after the copolymer of the present invention is formed, unreacted polybutene can be reacted with maleic anhydride to form thermal process PIBSA. PolyPIBSA prepared in a manner similar to Example 17B having a Saponification No. of 86 was charged to a reactor and heated to 204°C. A molar equivalent of maleic anhydride (43.3 g), relative to unreacted non-vinylidene polybutene, was added and the mixture heated to 232°C and held at this temperature for 4 hours. The temperature was reduced to 210°C and the pressure was reduced to 28 inches of mercury. The reduced pressure and temperature was maintained for one hour. Then the mixture was filtered. The product had a Saponification No. of 88.

---

72

01 WHAT IS CLAIMED IS:

02

03 1. A copolymer of an unsaturated acidic reactant and a  
04 high molecular weight olefin having a sufficient number  
05 of carbon atoms such that the resulting copolymer is  
06 soluble in lubricating oil and wherein at least 20  
07 percent of the total olefin comprises an  
08 alkylvinylidene isomer.

09

10 2. A copolymer according to Claim 1 wherein at least 50  
11 percent of the total olefin comprises an  
12 alkylvinylidene isomer.

13

14 3. A copolymer according to Claim 2 wherein said  
15 unsaturated acidic reactant is of the formula:

16



19

20 wherein X and X' are each independently selected from  
21 the group consisting of -OH, -Cl, -O-lower alkyl and  
22 when taken together, X and X' are -O-.

23

24 4. A copolymer according to Claim 3 having an average  
25 degree of polymerization greater than 1.0.

26

27 5. A copolymer according to Claim 4 wherein said olefin  
28 has an average molecular weight of about 500 to about  
29 5000.

30

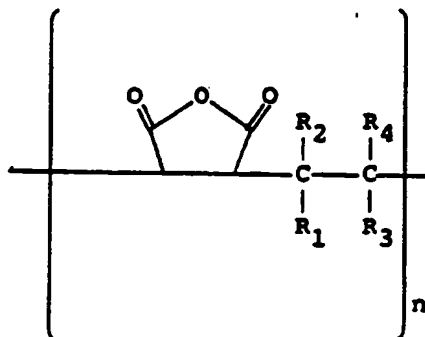
31 6. A copolymer according to Claim 5 wherein said olefin is  
32 polyisobutene.

33

34

73

- 01 7. A copolymer according to Claim 6 having an average  
 02 degree of polymerization of about 1.5 to about 10.  
 03
- 04 8. A copolymer according to Claim 7 wherein said acidic  
 05 reactant comprises maleic anhydride.  
 06
- 07 9. A copolymer according to Claim 8 wherein said  
 08 polyisobutene has an average molecular weight of about  
 09 900 to about 2500.  
 10
- 11 10. A copolymer according to Claim 9 wherein at least about  
 12 70 percent of the total olefin comprises an  
 13 alkylvinylidene isomer.  
 14
- 15 11. A copolymer according to Claim 10 wherein said  
 16 alkylvinylidene isomer is methylvinylidene.  
 17
- 18 12. A copolymer of the formula:  
 19  
 20



31  
 32 wherein n is 1 or greater, and  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are  
 33 selected from hydrogen, lower alkyl of 1 to 6 carbon  
 34 atoms and high molecular weight polyalkyl; wherein

74

- 01        either  $R_1$  and  $R_2$  are hydrogen and one of  $R_3$  and  $R_4$  is  
02        lower alkyl and the other is high molecular weight  
03        polyalkyl, or  $R_3$  and  $R_4$  are hydrogen and one of  $R_1$  and  
04         $R_2$  is lower alkyl and the other is high molecular  
05        weight polyalkyl.  
06
- 07    13.    A copolymer according to Claim 12 wherein said high  
08        molecular weight polyalkyl comprises a polyisobutyl  
09        group of at least about 50 carbon atoms.  
10
- 11    14.    A copolymer according to Claim 13 wherein said  
12        polyisobutyl group has an average molecular weight of  
13        about 500 to 5000.  
14
- 15    15.    A copolymer according to Claim 14 wherein said  
16        polyisobutyl group has an average molecular weight of  
17        about 900 to 2500.  
18
- 19    16.    A copolymer according to Claim 15 wherein having an  
20        average degree of polymerization of about 1.1 to about  
21        20.  
22
- 23    17.    A copolymer according to Claim 16 wherein said lower  
24        alkyl is methyl.  
25
- 26    18.    A product prepared by the process which comprises  
27        reacting a higher molecular weight olefin wherein at  
28        least about 20 percent of the total high molecular  
29        weight olefin comprises an alkylvinylidene isomer and  
30        wherein said high molecular weight olefin has a  
31        sufficient number of carbon atoms that said product is  
32        soluble in lubricating oil with an unsaturated acidic  
33        reactant in the presence of a free radical initiator.  
34

- 01 19. A product prepared as in the process of Claim 18  
02 wherein said unsaturated acidic reactant is of the  
03 formula:  
04



- 07 wherein X and X' are each independently selected from  
08 the group consisting of -OH, -Cl, -O-lower alkyl and  
09 when taken together, R and R' are -O-.  
10

- 11 20. A product prepared as in the process of Claim 19  
12 wherein at least 50 percent of the total olefin  
13 comprises an alkylvinylidene isomer.  
14

- 15 21. A product prepared as in the process of Claim 20  
16 wherein said high molecular weight olefin has an  
17 average molecular weight of about 500 to about 5000.  
18

- 19 22. A product prepared as in the process of Claim 21  
20 wherein said high molecular weight olefin is  
21 polyisobutene.  
22

- 23 23. A product prepared as in the process of Claim 22 having  
24 an average degree of polymerization of about 1.5 to  
25 about 10.  
26

- 27 24. A product prepared as in the process of Claim 23  
28 wherein said acidic reactant is maleic anhydride and  
29 said alkylvinylidene isomer is methylvinylidene.  
30

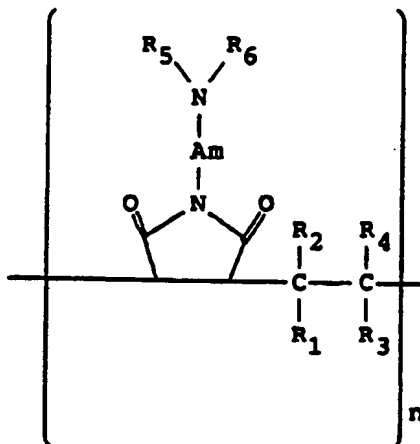
- 31 25. A copolymer according to Claim 1, 6 or 11 having a  
32 characteristic infrared succinic anhydride stretch in  
33 the range of about  $1775 \text{ cm}^{-1}$  to about  $1784 \text{ cm}^{-1}$  as  
34 measured by infrared spectroscopy.

76

- 01 26. A polysuccinimide prepared by reacting a copolymer  
02 according to Claim 1, 6 or 11 with a polyamine having  
03 at least one basic nitrogen atom.  
04  
05
- 06 27. A polysuccinimide according to Claim 26 having a  
07 characteristic infrared succinimide stretch in the  
08 range of about  $1697\text{ cm}^{-1}$  to about  $1703\text{ cm}^{-1}$  as measured  
09 by infrared spectroscopy.  
10
- 11 28. A polysuccinimide according to Claim 26 wherein said  
12 polyamine has from about 2 to about 12 amine nitrogen  
13 atoms and from about 2 to about 40 carbon atoms.  
14
- 15 29. A polysuccinimide according to Claim 28 wherein said  
16 polyamine has the formula  $\text{H}_2\text{N}(\text{YNH})_p\text{H}$  wherein Y is  
17 alkylene of 2 to 6 carbon atoms and p is an integer  
18 from 1 to 6.  
19
- 20 30. A polysuccinimide according to Claim 29 wherein the  
21 charge mole ratio of polyamine to succinic groups in  
22 copolymer is from about 1 to about 0.1.  
23
- 24 31. A polysuccinimide according to Claim 29 wherein the  
25 charge mole ratio of polyamine to succinic groups in  
26 copolymer is about 0.5.  
27  
28  
29  
30  
31  
32  
33  
34

77

01 32. A compound of the formula:

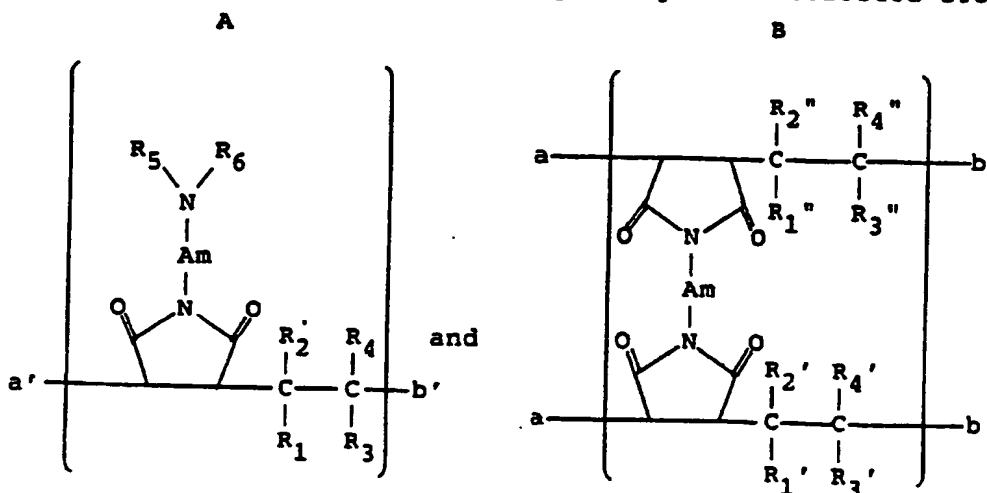


15 wherein n is one or greater, Am has from about 0 to  
16 about 10 amine nitrogen atoms and from about 2 to about  
17 40 carbon atoms; and R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are selected  
18 from hydrogen, lower alkyl of 1 to 6 carbon atoms and  
19 high molecular weight polyalkyl; wherein either R<sub>1</sub> and  
20 R<sub>2</sub> are hydrogen and one of R<sub>3</sub> and R<sub>4</sub> is lower alkyl and  
21 the other is high molecular weight polyalkyl, or R<sub>3</sub> and  
22 R<sub>4</sub> are hydrogen and one of R<sub>1</sub> and R<sub>2</sub> is lower alkyl and  
23 the other is high molecular weight polyalkyl; and R<sub>5</sub>  
24 and R<sub>6</sub> are independently hydrogen, lower alkyl of 1 to  
25 6 carbon atoms, phenyl or taken together are alkylene  
26 of 3 to 6 carbon atoms to give a ring.

27  
28 33. A compound according to Claim 32 wherein said high  
29 molecular weight polyalkyl comprises a polyisobutyl  
30 group of at least about 50 carbon atoms.

31  
32 34. A compound according to Claim 33 wherein said  
33 polyisobutyl group has an average molecular weight of  
34 about 500 to about 5000.

- 01 35. A compound according to Claim 34 wherein Am has the  
 02 formula  $[(ZNH)pZ']$  wherein Z and Z' are independently  
 03 alkylene of from 2 to 6 carbon atoms and p is an  
 04 integer from 1 to 6, and  $R_5$  and  $R_6$  are hydrogen.  
 05  
 06 36. A compound according to Claim 35 having an average  
 07 degree of polymerization of about 1.1 to about 20.  
 08  
 09 37. A compound according to Claim 36 wherein said  
 10 polyisobutyl group has an average molecular weight of  
 11 about 900 to about 2500.  
 12  
 13 38. A compound according to Claim 37 wherein said lower  
 14 alkyl is methyl.  
 15  
 16 39. A compound according to Claim 38 having an average  
 17 degree of polymerization of about 1.5 to about 10.  
 18  
 19 40. A compound according to Claim 37 wherein Z and Z' are  
 20 ethylene and p is 2, 3 or 4.  
 21  
 22 41. A random polysuccinimide comprising units selected from





- 01  
02 wherein Am is a linking group having from about 0 to 10  
03 amine nitrogen atoms and from about 2 to 40 carbon  
04 atoms;  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_1'$ ,  $R_2'$ ,  $R_3'$ ,  $R_4'$ ,  $R_1''$ ,  $R_2''$ ,  
05  $R_3''$ , and  $R_4''$  are selected from hydrogen, lower alkyl of  
06 one to 6 carbon atoms and high molecular weight poly-  
07 alkyl; wherein either  $R_1$  and  $R_2$  are hydrogen and one of  
08  $R_3$  and  $R_4$  is lower alkyl and the other is polyalkyl, or  
09  $R_3$  and  $R_4$  are hydrogen and one of  $R_1$  and  $R_2$  is lower  
10 alkyl and the other is polyalkyl; either  $R_1'$  and  $R_2'$   
11 are hydrogen and one of  $R_3$  and  $R_4$  is lower alkyl and  
12 the other is polyalkyl, or  $R_3'$  and  $R_4'$  are hydrogen and  
13 one of  $R_1'$  and  $R_2'$  is lower alkyl and the other is  
14 polyalkyl; and either  $R_1''$  and  $R_2''$  are hydrogen and one  
15 of  $R_3''$  and  $R_4''$  is lower alkyl and the other is poly-  
16 alkyl or  $R_3''$  and  $R_4''$  are hydrogen and one of  $R_1''$  and  
17  $R_2''$  is lower alkyl and the other is polyalkyl;  $R_5$  and  
18  $R_6$  are independently hydrogen, lower alkyl of 1 to 6  
19 carbon atoms, phenyl or taken together are alkylene of  
20 3 to 6 carbon atoms to give a ring; and a, a', b and b'  
21 are sites for a covalent bond; provided that at least  
22 one a or a' site of each unit is covalently bonded to a  
23 b or b' site.  
24
- 25 42. A random polysuccinimide according to Claim 41 wherein  
26 said high molecular weight polyalkyl comprises a  
27 polyisobutyl group of at least about 50 carbon atoms.  
28
- 29 43. A random polysuccinimide according to Claim 42 wherein  
30 said polyisobutyl group has an average molecular weight  
31 of about 500 to 5000.  
32
- 33 44. A random polysuccinimide according to Claim 43 wherein  
34 Am has the formula  $-[(ZNH)_pZ']-$  wherein Z is alkylene

- 01 of 2 to 6 carbon atoms, Z' is alkylene of 2 to 6 carbon  
02 atoms and p is an integer from 0 to 5, and R<sub>5</sub> and R<sub>6</sub>  
03 are hydrogen.  
04
- 05 45. A random polysuccinimide according to Claim 44 wherein  
06 the average sum of A and B units is from about 2 to  
07 about 50.  
08
- 09 46. A random polysuccinimide according to Claim 45 wherein  
10 said polyisobutyl group has an average molecular weight  
11 of about 900 to about 2500.  
12
- 13 47. A random polysuccinimide according to Claim 46 wherein  
14 said lower alkyl is methyl.  
15
- 16 48. A random polysuccinimide according to Claim 47  
17 comprising from about 2 to about 10 times as many B  
18 units as A units.  
19
- 20 49. A random polysuccinimide according to Claim 48 wherein  
21 Z and Z' are ethylene and p is 1, 2 or 3.  
22
- 23 50. A fuel composition comprising a hydrocarbon boiling in  
24 a gasoline or diesel range and from about 30 to about  
25 5000 parts per million of a copolymer according to  
26 Claim 11.  
27
- 28 51. A fuel composition comprising a hydrocarbon boiling in  
29 a gasoline or diesel range and from about 30 to about  
30 5000 parts per million of an polysuccinimide according  
31 to Claim 29.  
32
- 33 52. A fuel composition comprising a hydrocarbon boiling in  
34 a gasoline or diesel range and from about 30 to about

- 01        5000 parts per million of an compound according to  
02        Claim 40.  
03
- 04    53.   A fuel composition comprising a hydrocarbon boiling in  
05        a gasoline or diesel range and from about 30 to about  
06        5000 parts per million of an random polysuccinimide  
07        according to Claim 49.  
08
- 09    54.   A fuel concentrate comprising an inert stable  
10        oleophilic organic solvent boiling in the range of  
11        150°F to 400°F and from about 5 to about 50 weight  
12        percent of a copolymer according to Claim 11.  
13
- 14    55.   A fuel concentrate comprising an inert stable  
15        oleophilic organic solvent boiling in the range of  
16        150°F to 400°F and from about 5 to about 50 weight  
17        percent of a polysuccinimide according to Claim 29.  
18
- 19    56.   A fuel concentrate comprising an inert stable  
20        oleophilic organic solvent boiling in the range of  
21        150°F to 400°F and from about 5 to about 50 weight  
22        percent of a compound according to Claim 40.  
23
- 24    57.   A fuel concentrate comprising an inert stable  
25        oleophilic organic solvent boiling in the range of  
26        150°F to 400°F and from about 5 to about 50 weight  
27        percent of a random polysuccinimide according to  
28        Claim 49.  
29
- 30    58.   A lubricating oil composition comprising an oil of  
31        lubricating viscosity and a dispersant effective amount  
32        of a copolymer according to Claim 11.  
33  
34
-

- 01 59. A lubricating oil composition comprising an oil of  
02 lubricating viscosity and a dispersant effective amount  
03 of a polysuccinimide according to Claim 29.  
04
- 05 60. A lubricating oil composition comprising an oil of  
06 lubricating viscosity and a dispersant effective amount  
07 of a compound according to Claim 40.  
08
- 09 61. A lubricating oil composition comprising an oil of  
10 lubricating viscosity and a dispersant effective amount  
11 of a random polysuccinimide according to Claim 49.  
12
- 13 62. A lubricating oil concentrate comprising from about 90  
14 to about 50 weight percent of an oil of lubricating  
15 viscosity and from about 10 to about 50 weight percent  
16 of a copolymer according to Claim 11.  
17
- 18 63. A lubricating oil concentrate comprising from about 90  
19 to about 50 weight percent of an oil of lubricating  
20 viscosity and from about 10 to about 50 weight percent  
21 of a polysuccinimide according to Claim 29.  
22
- 23 64. A lubricating oil concentrate comprising from about 90  
24 to about 50 weight percent of an oil of lubricating  
25 viscosity and from about 10 to about 50 weight percent  
26 of a compound according to Claim 40.  
27
- 28 65. A lubricating oil concentrate comprising from about 90  
29 to about 50 weight percent of an oil of lubricating  
30 viscosity and from about 10 to about 50 weight percent  
31 of a random polysuccinimide according to Claim 49.  
32
- 33 66. A product prepared by the process which comprises  
34 reacting a polysuccinimide according to Claim 26 having

83

- 01       at least one primary or secondary amine group with a  
02       cyclic carbonate or a linear mono- or poly-carbonate.  
03  
04   67.   The product according to Claim 66, wherein the  
05       polysuccinimide is reacted with a cyclic carbonate.  
06  
07   68.   The product according to Claim 67, wherein the cyclic  
08       carbonate is ethylene carbonate.  
09  
10   69.   A product prepared by the process which comprises  
11       reacting a polysuccinimide according to Claim 26 with a  
12       boron compound selected from the group consisting of  
13       boron oxide, boron halide, boric acid and esters of  
14       boric acid.  
15  
16   70.   The product according to Claim 69, wherein the boron  
17       compound is boric acid.  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34
-

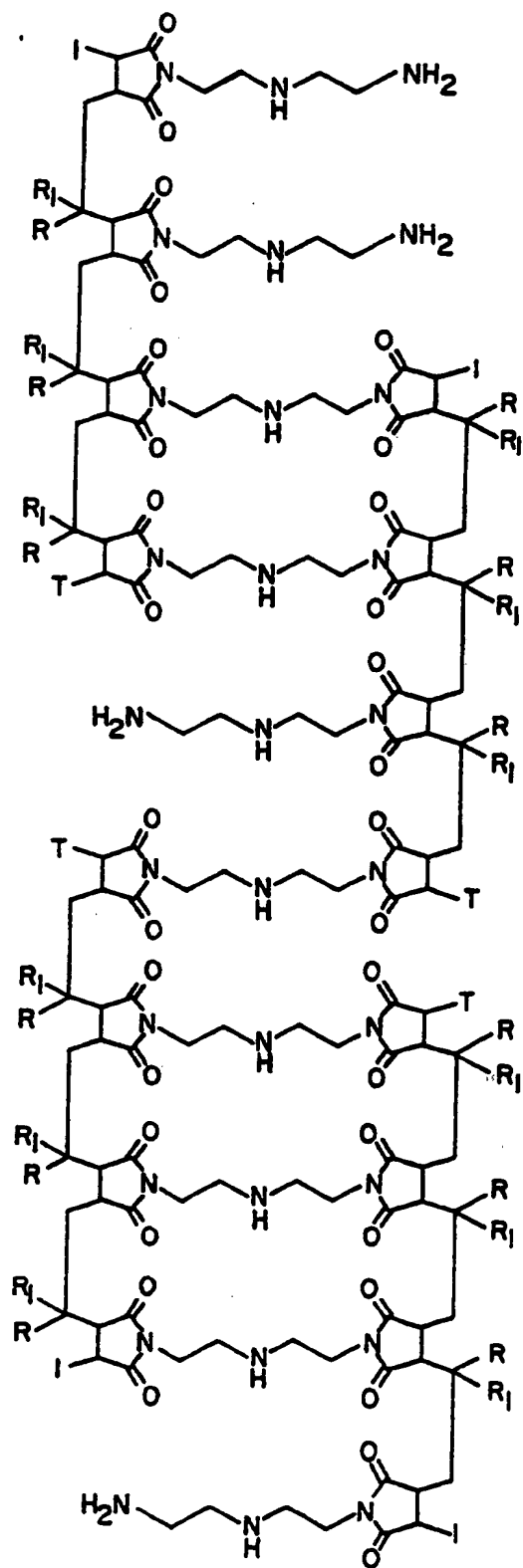


FIG. 1.

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US89/04270

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT CL <sup>4</sup> : C07C 55/00,69/34; C07D,307/34; C10M 129/93; C10L 1/18,1/22		
US CL: 562/590,596; 560/190,204; 549/233,252; 526/262; 548/546,547; 252/56D,51.5A 44/62 <sup>63</sup>		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
US	562/590,596; 560/190,204; 549/233,252; 526/262; 548/546,547; 252/56D,51.5A; 44/62,63	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b>		
Category <sup>9</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
<u>X</u> <u>Y</u>	US, A, 4,548,725, (BRIDGER) 22 October 1985 See entire document	1-8,12,14,18-23, 25,58,62,16 9-11,13,15,17,24
<u>X</u> <u>Y</u>	US, A, 4,526,950, (GRAVA) 02 July 1985 See entire document	1-4,8,10,12,16,18- 20,23,25,7 5,6,9,11,13-15,17 21,22,24
<u>X</u> <u>Y</u>	US, A, 4,416,668, (THOMPSON) 22 November 1983 See entire document	26-36,39,40,51, 52,55,56 37,38
<u>X</u> <u>Y</u>	US, A, 3,677,725, (ANDRESS, JR) 18 July 1972 See entire document	1-4,7,8,12,16,18- 20,23,25,50,54 5,6,9-11,13-15,17 21,22,24
<u>X</u> <u>Y</u> P	JP, A, 63-270671, (MITSUBISHI) 08 Novmeber 1988 See entire document	1-8,12-14,16,18- 23,25,58,62 9-11,15,17,24
A	US, A, 4,612,132 (WOLLENBERG ET AL) 16 September 1986, See entire document	66,67,68
<p>* Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
12 December 1989		10 JAN 1990
International Searching Authority		Signature of Authorized Officer
ISA/US		<i>Allen H. S. [Signature]</i>

## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	US,A, 4,359,325, (DAWANS ET AL) 16 November 1982 See entire document	1-70
A	US,A, 4,055,581, (HOPKINS ET AL) 25 October 1977 See entire document	1-70
A	US,A, 3,720,733, (RINKLER ET AL) 13 March 1973 See entire document	1-70
A	US,A, 2,977,334, (ZOPP, JR ET AL) 28 March 1961 See entire document	1-70
A	SU,A, 900,599, (A MED POLIO VIRUS) 15 January 1985 See entire document	1-70

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers \_\_\_\_\_, because they relate to subject matter <sup>12</sup> not required to be searched by this Authority, namely:
2. ☐ Claim numbers \_\_\_\_\_, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out <sup>13</sup>, specifically:
3. ☐ Claim numbers \_\_\_\_\_, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.